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THE NATURE OF THE THERMAL AGITATION IN CRYSTALS

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1. Introduction

The present memoir concerns itself with a problem of fundamental importance in the physics of the solid state, namely the determination of the nature of the atomic movements which constitute the thermal agitation in a crystal. It would be no exaggeration to say that on our taking the correct view of the nature of these movements depends the possibility of our understanding the physical behaviour of crystals aright, not only in the thermal field but also in diverse other fields, as for example their spectroscopic behaviour and the phenomena of X-ray diffraction in crystals. The problem is considered in this paper from two distinct points of view. The first method of approach is to examine the basic experimental facts in the light of fundamental physical principles and to draw the inferences following logically therefrom. The second method of approach is the analytical investigation of the problem on the basis of classical mechanics and the general principles of thermodynamics and the quantum theory. The result in either case is to show that the ideas underlying the well-known specific heat theory of Debye and the lattice dynamics of Born and his collaborators are untenable. The picture of the thermal agitation in a crystal which emerges from the present investigation is fundamentally different from that postulated in the theories of Debye and Born.

2. Some General Considerations

The identification on a quantitative basis of the thermal energy of a crystal with the energy of atomic oscillations rests on two fundamental ideas; (*a*) that the oscillators can be enumerated, their total number being three times the number of atoms comprised in the crystal; (*b*) that the energy of the oscillators is quantized and for any particular frequency has an average value which can be calculated with the aid of Boltzmann's theorem. We proceed to examine these ideas critically with a view to determine their precise significance as well as their implications.

The first of the two ideas referred to above is based on the fundamental theorem in classical mechanics which states that all the possible modes of

small vibration of a system of connected particles are superpositions of a set of normal modes, the number of such modes being the same as the number of degrees of dynamic freedom of the system, and further that in each such normal mode all the particles of the system have the same frequency of vibration and oscillate in the same or opposite phases. In the present context, therefore, the term oscillator must be considered as referring to a set of atoms vibrating in a normal mode, all of them having the same frequency and the same or opposite phases of vibration.

The second idea, namely that of averaging the energy of an oscillator, arises because of the chaotic nature of thermal agitation which involves energy fluctuations whose magnitude is determined by the frequency of the vibration. The theorem of Boltzmann which enables the average to be calculated is a description in statistical form of the behaviour of the individual units in an assembly consisting of an immense number of such units which are physically identical but differ in their energy states and being in a position to exchange energy with each other form a system in thermodynamic equilibrium. In the present context, the units are the oscillators defined in the preceding paragraph. Hence, if the application of Boltzmann's theorem is to be legitimate, it is necessary to postulate that in the crystal is present an assembly of this nature, *viz.*, a great number of individual oscillators all of which vibrate with the same frequency but are in the different energy states permitted by the quantum theory. For each separate frequency of oscillation, a fresh assembly of that nature is needed to enable the energy for each individual frequency to be separately averaged.

The foregoing theoretical picture of the thermal agitation agrees completely with the actual physical picture in the case under consideration. For, every crystal is itself an assembly of an immense number of similar and similarly situated groups of atoms, the internal vibrations of which can occur with one or another of the characteristic frequencies of the group. The energy of vibration of a group with any one of these frequencies may have any of the series of values allowed by the quantum theory and hence would vary from group to group in an entirely unpredictable manner within the crystal. Such a picture would be in perfect harmony with the basic notions of thermodynamics, but would be wholly irreconcilable with any theory which seeks to identify the energy of thermal agitation with the energy of regular wave propagation in the crystal. But this latter idea is precisely what forms the basis of the specific heat theories of Debye and Max Born. It follows that these theories are fundamentally misconceived and must therefore fail, together with all their consequences.

3. The Normal Modes of Vibration

The normal modes of vibration of the atomic groupings in the crystal referred to above may be determined and enumerated without any difficulty. It is obviously not permissible in this connection to regard the unit cell in the crystal structure as isolated from the rest of the crystal. For, any oscillation which occurs in a particular cell will necessarily communicate itself immediately to the surrounding cells and set the latter in vibration with the same frequency. Hence, to ascertain the normal modes of vibration, we have to consider vibrations extending over domains whose dimensions are at least as large as the range of the inter-atomic forces. Further, to ensure that the oscillations persist unchanged in character, it is necessary to assume that the oscillation in each of the unit cells included within such a domain is similar and similarly related to the oscillations in the cells surrounding it.

Remembering that in a normal mode the oscillations of all the particles have the same frequency and the same or opposite phase, the foregoing requirements lead us to the following description of the normal modes of vibration: In any normal mode, the oscillations of equivalent atoms in adjoining cells have the same amplitude of vibration but their phases are either the same or the opposite in the cells adjacent to one another along one, two or all three of the axes of the lattice structure. Thus there are $2 \times 2 \times 2$ or 8 possible situations. As a consequence of the identity of the amplitudes of vibration of equivalent atoms in all the cells which need to be considered, the $3p$ equations of motion of the p atoms in any particular cell contain only $3p$ unknowns. Accordingly, it becomes possible to solve the equations completely and determine the $3p$ normal modes and the corresponding frequencies of vibration. As there are eight different situations in respect of the phases of vibration, the equations of motion would necessarily be different in each of them. Accordingly we have $3p \times 8$ or $24p$ normal modes and frequencies of vibration.

An alternative and convenient way of describing the normal modes is to consider a supercell of the lattice whose dimensions are twice as large in each direction as the unit cell. Such a supercell would contain $8p$ atoms and the total number of degrees of freedom associated therewith would be $24p$, and this is the same as the number of normal modes permissible. We may therefore describe these modes as the vibrations of the atoms comprised in the supercell. When this description is adopted, it becomes immediately evident that three of these modes would represent simple translations of the supercell and would therefore have to be excluded in enumerating the internal vibrations of the supercell. We have then left only $(24p - 3)$ normal modes of vibration properly so-called.

4. WAVE PROPAGATION IN CRYSTAL LATTICES

As is well known, the classical theory of elasticity leads to the conclusion that three types of waves can be propagated in any given direction within crystal with the velocities determined by the density of the material and certain linear combinations of its elastic constants. The analysis which leads to this result regards the volume elements of the crystal as simple mass particles whose equations of motion can be written down in terms of the tractive forces arising from the elastic strains. Hence the theory and its consequences would cease to be applicable when these assumptions are invalid and the position would then have to be considered afresh from the atomistic standpoint. A formal investigation on the latter basis shows that only in the limiting case of very low frequencies and of correspondingly long waves are the results of the classical theory of elasticity valid. When we enter the region of the higher frequencies, the phase velocity and the group velocity diverge from each other and the very significant result emerges that the group velocity vanishes for $(24\,p - 3)$ modes of vibration of the lattice. These modes are found to be identical with the $(24\,p - 3)$ normal modes referred to in the foregoing section.

To avoid breaking the thread of the argument, the detailed dynamical investigation which has been worked out by Dr. K. S. Viswanathan is printed as an appendix to this memoir. It will therefore suffice here to comment on the significance of the results there derived by him. As is very well understood, it is the group velocity which is physically significant in all considerations regarding wave-propagation, since it is a measure of the rate of energy transport in the medium. The vanishing of the group velocity for the whole series of characteristic frequencies of atomic vibration signifies that there is no wave propagation in the real or physical sense of the term when we are considering oscillations in which the interatomic displacements play a significant role. It follows that considerations of the kind used in the classical theory of elasticity to ascertain the normal modes of vibration of a solid body of finite extension are entirely out of place in the atomistic problem. But it is precisely such considerations that are employed in the theories of Debye and Born to describe and enumerate the movements which they identify with the thermal agitation. Thus, even on the basis of the classical mechanics, the ideas underlying those theories are unsustainable and they have therefore to be laid aside as being completely unreal.

5. THE FREQUENCY SPECTRUM OF THE THERMAL AGITATION

We may sum up what has been said in the foregoing pages by the statement that the energy of the thermal agitation in a crystal may be identified

with the energy of an immense number of atomic oscillators which together fill up the volume of the crystal, the individual oscillators being in the various states of excitation corresponding to each of the $(24p-3)$ frequencies common to them all, supplemented by the energy of the low frequency oscillations which the three omitted degrees of freedom represent. These $(24p-3)$ frequencies correspond to modes of vibration which are related to the structure of the crystal in precisely definable terms. It will be seen that this description of the thermal agitation bears no resemblance whatever to that envisaged in the theories of Debye and Born; these authors identify the energy of the thermal agitation with the energy of waves in immense numbers traversing the crystal in all directions and having frequencies which are all different from one another, the energy of the wave of any particular frequency as well as the sum total of the energy of all the waves taken together being distributed uniformly over the volume of the crystal.

It is noteworthy that in his fundamental paper of 1907 introducing the quantum theory of specific heats, Einstein derived his expression for the average energy of an oscillator of given frequency assuming, as is indeed necessary for applying Boltzmann's theorem, that the crystal is an assembly of an immense number of oscillators all having the same frequency but in different energy states and in thermodynamic equilibrium with each other. The theories of Debye and Born make use of Einstein's expression for the average energy of an oscillator, while on the other hand the frequencies of the waves with which they identify the thermal agitation are all different from each other. Thus it will be seen that there is no logical consistency in their approach to the specific heat problem. Further, the uniform distribution of the thermal energy through the whole volume of the crystal which such identification demands is irreconcilable with the fundamental ideas regarding the nature of the thermal energy of material bodies inherent in the Second Law of Thermodynamics, namely, that the distribution of the energy over the volume of the crystal should exhibit fluctuations which are the more violent the higher the frequency of vibration.

The foregoing comments do not by any means traverse all the arguments and assumptions on which the theories of Debye and Born are based. One of the basic objections to their method of approaching the specific heat problem is that since wave motions involve progressive changes of phase along the direction of propagation and may have any frequency assigned to them, they can neither be treated as normal modes nor enumerated. The theories of Debye and Born seek to escape this difficulty by postulating that the number of wave motions is identical with the number of degrees of freedom of the system, while the choice of wavelengths is determined by still

another postulate, *e.g.*, the so-called postulate of the cyclic lattice which is claimed to represent the effect of the external boundary of the crystal. Since it is obviously impossible to formulate any boundary conditions for the atomic movements at the external surface of a crystal, the procedure is clearly artificial. But that it is also fallacious becomes evident when we remark that the characteristic modes and frequencies of the atoms in the interior of the crystal are determined exclusively by the structure of the crystal and by the interatomic forces whose range is exceedingly small and hence there exists no justification whatever for the assumption which is inherent in the postulate that these modes and frequencies are influenced by the presence of an external boundary.

6. THE SPECTROSCOPIC BEHAVIOUR OF CRYSTALS

It is not proposed in this memoir to discuss how the ideas set forth in it impinge on various aspects of crystal physics. We shall however make a brief reference to those cases in which facts already well established illustrate the validity of the conclusions reached in it.

As Einstein emphasized in his fundamental paper of 1907, the theory of the specific heats of crystals stands in the closest relation to their spectroscopic behaviour. In seeking to explain the data then available for the case of diamond, he made the simplifying assumption that all the oscillators in that crystal have a single common frequency. He recognized however, that in general a crystal would possess several characteristic frequencies and that the expression for its specific heat would involve a summation over them all. In the particular case of diamond, the $(24\,p-3)$ frequencies indicated by the present theory are reduced from 45 to 9 in number by reason of the cubic symmetry of the crystal. One of these 9 frequencies represents the triply degenerate oscillation of the two lattices of carbon atoms against each other, while the other eight represent either the longitudinal or the transverse oscillations of the layers of carbon atoms in the cubic and octahedral planes of the crystal. In numerous papers published in these *Proceedings* in recent years, it has been shown that all these nine frequencies can be ascertained by spectroscopic observation and that the specific heat of diamond can be successfully evaluated with the aid of the data thus obtained.

But the case of diamond does not stand alone in this respect. In recent years, the spectroscopic behaviour of numerous crystals have been studied by diverse methods, *e.g.*, the scattering of light, absorption in the visible, ultra-violet and infra-red regions of the spectrum, and in particular cases, also their luminescence. The whole of the evidence which has thus come

to hand indicates that the vibration spectrum of a crystal consists of a discrete set of monochromatic frequencies and that where there is any departure from this state of affairs, an adequate explanation is forthcoming.

7. X-Ray Diffraction in Crystals

That the atomic vibrations in crystals appear with precisely defined frequencies and with modes bearing a precise geometric relationship to the architecture of the crystal has a most important bearing on the subject of the diffraction of X-rays by crystals. Here again, a particularly striking illustration is furnished by the case of diamond. When a plate of this crystal is traversed by a narrow pencil of X-rays and the resulting Laue pattern is recorded on a photographic plate, it is found that in addition to the usual Laue spots, other sets of sharply defined spots appear on the plate, corresponding to each of the monochromatic components in the incident X-radiation. This phenomenon which was discovered in the year 1940 by Dr. Nilakantan and the present writer using octahedral cleavage plates of diamond has since been thoroughly re-investigated at this Institute by Mr. Jayaraman and the writer. The results are found to be in complete accord with the hypothesis that the incident X-radiation excites the triply degenerate oscillation of the two lattices of carbon atoms in the crystal against each other. These movements occur along the directions of the three cubic axes and as a consequence, all the lattice planes of the crystal are disturbed, giving rise to dynamic X-ray reflections by them. *Three* sharply-defined spots corresponding to each monochromatic component in the incident X-ray beam are demanded by the theory for the dynamic reflections by each of the (111) planes of the crystal, since these planes are equally inclined to the cubic axes. These reflections are actually observed in the directions indicated by the theory with suitable settings of the crystal. Other sets of lattice planes in the crystal also give dynamic reflections in the directions demanded by the theory, but since such planes are unequally inclined to the three cubic axes which are the directions of movement of the atoms in the excited oscillations, they are not all equally conspicuous.

Here again the case of diamond does not stand by itself, since analogous phenomena are also exhibited by other crystals. But it is not necessary here to enter into the details of these cases.

8. Summary

The principles of thermodynamics and of the quantum theory indicate that the thermal energy in a crystal is identifiable with the energy of an

immense number of atomic oscillators which have their frequencies of vibration in common but are in different states of excitation. Dynamical investigation of the problem shows that if the crystal contains p interpenetrating Bravais lattices of atoms, there are $(24p-3)$ frequencies of vibration common to all the oscillators. An investigation of the propagation of waves in crystal lattices shows that the results of the classical theory of elasticity are valid only in the limiting case of very low frequencies and proves further that the group velocity of the waves vanishes for $(24p-3)$ frequencies which may accordingly be identified as the characteristic frequencies of atomic vibration in the crystal. Since there is no wave-propagation in the real or physical sense except in the very lowest range of frequencies, the identification of the thermal energy with the energy of waves traversing the crystal in all directions and having frequencies all different from one another which forms the basis of the specific heat theory of Debye and of Born's lattice dynamics ceases to be justifiable. Other aspects of these latter theories are also examined and it is shown that the assumptions which they involve are untenable and that in consequence the theories have no claim to validity. The experimental results which confirm that the atomic oscillators have specific frequencies in common and modes of vibration specifically related to the crystal structure are briefly set out.

APPENDIX

We shall consider the most general case of a crystal whose structure includes p interpenetrating Bravais lattices, all of which are geometrically similar and similarly situated in the crystal arrangement. An unit cell of the crystal will therefore contain p atoms whose masses we shall denote by $m_1, m_2, \ldots . m_p$.

Since a crystal is triply periodic in space, any unit cell can be reached from any other cell of the crystal by the application of three primitive translations or integral multiples of them. We denote the three primitive translations by the three vectors $\mathbf{d}_1$, $\mathbf{d}_2$ and $\mathbf{d}_3$. In the same way, we denote the three primitive vectors of the reciprocal lattice by $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$. In what follows, the symbols $\mathbf{s}$ and σ will be used to denote particular cells in the crystal structure while r and ρ will indicate particular atoms in the unit cell; X, Y, Z are three mutually perpendicular directions chosen as the co-ordinate axes along which the displacements of the atoms from their equilibrium positions are resolved. We represent the displacement-components of any atom, say the rth atom in the $\mathbf{s}$th cell, by means of the symbols q_{xrs}, q_{yrs}, q_{zrs}. We can now write the equations of motion of the atoms in the $\mathbf{s}$th cell and they take the form

$$-m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k_{xrs}^{y\rho\sigma} q_{y\rho\sigma} \quad \begin{pmatrix} x = \mathrm{X, Y, Z} \\ r = 1, 2, \ldots . p \end{pmatrix} \tag{1}$$

The force constant $k_{xrs}^{y\rho\sigma}$ occurring in (1) expresses the proportionality existing between the x-component of the force acting on the atom $(r, \mathbf{s})$ to the displacement in the y-direction of the atom (ρ, σ) which gives rise to this force.

Since the crystal is composed of p different Bravais lattices of atoms, we can reasonably expect a wave of a given wavelength and frequency to be propagated with different amplitudes inside the p different lattices. To solve the set of equations (1), we therefore assume solutions of the form

$$\begin{aligned} q_{xrs} &= \mathrm{A}_{xr}\, e^{i(\omega t - a.s)} \\ &= \mathrm{A}_{xr}\, e^{\frac{2\pi i}{\lambda}(\nu t - e.s)} \end{aligned} \quad \begin{pmatrix} x = \mathrm{X, Y, Z} \\ r = 1, 2, \ldots . p \end{pmatrix} \tag{2}$$

which are plane waves of wavelength λ and circular frequency ω propagating in the direction of the vector $\mathbf{e}$ of the crystal. If we resolve the wave-vector $\mathbf{a}$ along the three axes of the reciprocal lattice and write $\mathbf{a} = \theta_1\mathbf{b}_1 + \theta_2\mathbf{b}_2 + \theta_3\mathbf{b}_3$ then the equations (2) can alternatively be written as

$$q_{xrs} = \mathrm{A}_{xr}\, e^{i(\omega t - s_1\theta_1 - s_2\theta_2 - s_3\theta_3)} \tag{2'}$$

where s_1, s_2 and s_3 are the components of **s** along the three Bravais axes of the crystal. Substituting the equations (2) in (1), we obtain

$$m_r\omega^2 A_{xr} = \sum_{y\rho} A_{y\rho} \left(\sum_{\sigma} k^{yrs}_{y\rho\sigma}\, e^{ia.\sigma - s}\right) \quad \begin{pmatrix} x = X, Y, Z \\ r = 1, 2, \ldots . p \end{pmatrix} \qquad (3)$$

Equations (3) are a set of $3p$ equations in the $3p$ amplitudes A_{x1}, A_{y1}, A_{z1}, A_{x2},.... A_{zn} of the waves. By eliminating the amplitudes from these homogeneous equations, we can obtain a determinental equation containing $3p$ rows and $3p$ columns whose elements are the coefficients of the various $A_{y\rho}$'s in the equations (3). By expanding this determinant, we can rewrite this equation in the form

$$s_0\omega^{6p} + s_1\omega^{6p-2} + \ldots\ldots + s_{3p} = 0 \qquad (4)$$

in which s_0, s_1, ...s_{3p} are functions of the coefficients of the amplitudes in the equations (3), and hence are also functions of the wave-vector of the waves. The roots of the equations (4) are consequently functions of the wavelengths of the waves, in other words, the waves are dispersive. Since an algebraic equation of degree $3p$ has $3p$ roots, for each value of a we obtain $3p$ permissible values for ω which are the roots of (4). Thus there are $3p$ waves of a given wavelength moving in any direction of the crystal.

We shall now consider any one of the $3p$ roots of the equation (4). If this is denoted by ω_k^2, then ω_k^2 expressed as a function of the wave-vector **a** has the following properties:

(i) ω_k^2 is a periodic function of θ_1, θ_2 and θ_3 with periods 2π for each one of these variables;

(ii) ω_k^2 is a real function of θ_1, θ_2 and θ_3;

(iii) ω_k^2 is an even function of the wave-vector **a** (*i.e.*), $\omega_k^2(\mathbf{a}) = \omega_k^2(-\mathbf{a})$.

Condition (i) follows from the fact that the coefficients of the amplitudes in (3) are of the form

$$\sum_{\sigma} k^{y\rho\sigma}_{xrs} \text{ exp. } i\mathbf{a}.(\sigma - \mathbf{s}) \text{ or}$$

$$\sum_{\sigma} k^{y\rho\sigma}_{xrs} \text{ exp. } i\,(\overline{\sigma_1 - s_1}\theta_1 + \overline{\sigma_2 - s_2}\theta_2 + \overline{\sigma_3 - s_3}\theta_3$$

and hence are periodic functions of θ_1, θ_2 and θ_3 with periods 2π for each of them. The frequencies of the waves which are functions only of these coefficients are therefore also periodic functions of θ_1, θ_2 and θ_3.

Condition (ii) can easily be understood from physical considerations. Condition (iii) follows from the fact that the frequency of a wave of given

wavelength and amplitude should be the same both for waves travelling in one and the opposite directions. Alternatively, these two conditions are consequences of the hermitian property of the coefficients of the amplitudes of the waves in the right-hand side of the equations (3).

Since $\omega_k{}^2$ is a periodic function of θ_1, θ_2 and θ_3 we can express it as a three-dimensional Fourier-series in the form

$$\omega_k{}^2 = \sum_{n_1,} \sum_{n_2,} \sum_{n_3=-\infty}^{+\infty} A_{n_1 n_2 n_3} \, e^{i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)} \tag{5}$$

where the summation extends over all integral values of n_1, n_2 and n_3 from $-\infty$ to $+\infty$.

If we use a single symbol $\mathbf{n}$ to denote the triplet $(n_1\, n_2\, n_3)$ we can rewrite (5) also in the form

$$\omega_k{}^2 = \sum_{\mathbf{n}} A_n \, e^{i\mathbf{a}.\mathbf{n}} \tag{6}$$

Since $\omega_k{}^2$ is real, the coefficients of $e^{i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)}$ and $e^{-i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)}$ in (5) should be complex conjugates. Hence we have

$$A_n = \bar{A}_{-n} \tag{7}$$

Now by writing $-\mathbf{a}$ for $\mathbf{a}$ in (6), we get

$$\omega_k{}^2(-\mathbf{a}) = \sum_{\mathbf{n}} A_n \, e^{-i\mathbf{a}.\mathbf{n}} \tag{8}$$

Since from condition (iii), $\omega_k{}^2(-\mathbf{a}) = \omega_k{}^2(\mathbf{a})$ we see by a comparison of (6) and (8) that

$$A_n = A_{-n} \tag{9}$$

Combining (7) and (9) we get

$$A_n = \bar{A}_{-n} = \bar{A}_n \tag{10}$$

or A_n is real.

We can therefore rewrite (5) as

$$\begin{aligned} \omega_k{}^2 &= A_{000} + 2 \sum A_{n_1 n_2 n_3} \cos(n_1\theta_1 + n_2\theta_2 + n_3\theta_3) \\ &= A_{000} + 2 \sum_{\mathbf{n}} A_n \cos \mathbf{a}.\mathbf{n} \end{aligned} \tag{11}$$

where the summation now is over all lattice points on and above any one of the lattice planes $\mathbf{d}_1 = 0$ or $\mathbf{d}_2 = 0$ or $\mathbf{d}_3 = 0$.

We shall assume that the series obtained by differentiating term by term the sum on the right-hand side of (11) converges uniformly for all values of θ_1, θ_2 and θ_3 in the interval $(0, 2\pi)$. Then, we have

$$2\omega_k \frac{d\omega_k}{da} = -2 \Sigma A_n \mathbf{e.n} \sin \mathbf{a.n} \tag{12}$$

Now, when θ_1, θ_2 and θ_3 each takes one of the values 0 or π, sin **a.n** (*i.e.*) sin $(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)$ is equal to zero. Hence if

$$\omega_k \neq 0 \tag{13}$$

for these values of θ_1, θ_2 and θ_3, we find from (12) that

$$\frac{d\omega_k}{da} = 0 \quad \text{whenever} \quad \theta_1 = 0 \text{ or } \pi; \quad \theta_2 = 0 \text{ or } \pi; \quad \theta_3 = 0 \text{ or } \pi \tag{14}$$

When $\theta_1 = 0$; $\theta_2 = 0$; $\theta_3 = 0$, it can be proved that three of the roots of (4) will become zero and hence the condition (13) is not satisfied. These are the limiting cases of elastic vibrations of long wavelength in the crystal and for them, since $\omega_k \to 0$ as $a \to 0$

$$\underset{a \to 0}{Lt} \frac{\omega_k}{a} = \frac{d\omega_k}{da} \quad (k = 1, 2, 3),$$

and therefore the group and wave velocities become identical with the velocities of propagation of the elastic vibrations in the crystal lattice.

The eight set of cases considered above now yield a total number of $24p$ frequencies. Leaving out of these the three degrees of freedom pertaining to pure translations and for which, as we have seen, the group velocity is non-zero being equal to its wave velocity, we get $(24p-3)$ frequencies for which the group velocity of the waves vanishes. The modes associated with these frequencies now possess a simple geometric description. By substituting the values of 0 or π for θ_1, θ_2 and θ_3 in (2′), it can easily be seen that in all the $(24p-3)$ cases referred to above, equivalent atoms in adjacent cells vibrate with the same amplitude and with the same or opposite phases along one, two or all three of the Bravais axes of the crystal. Since the group velocity is zero, any disturbance with these frequencies remains centred in the region of its origin. Further, the phase relationships for these $(24p-3)$ modes are exactly the same as those demanded for the normal vibrations of a connected system of particles.

THERMAL NEUTRON DISTRIBUTION DUE TO TIME-DEPENDENT FAST NEUTRON SOURCES IN NON-MULTIPLYING MEDIA

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Introduction

The distribution of thermal neutrons in a medium due to time-dependent fast neutron sources has been investigated on the age theory approximation by Gallone and Salvetti.[1] They have also obtained solutions for certain specific geometries using the 'symbolic operator' formalism.

In this paper we shall discuss the multigroup approximation for slowing down process and obtain the age theory approximation as a particular case resulting from the number of groups tending to infinity. It will be shown that the resolvant operator used by Gallone and Salvetti is just a particular case of a more general resolvant operator, namely the multi group resolvant operator. Finally we shall obtain explicit solutions on two group and age approximations for an infinite geometry as well as for a finite rectangular parallelopiped. The age theory expressions for a finite geometry have already been given by Gallone and Salvetti and are included here for completeness.

The Multigroup Approximation

In the multigroup approximation the neutron energy range from source to thermal is divided into a finite number of intervals. The neutrons in each interval of energy or 'group' obey the ordinary diffusion equation and it is assumed that the neutrons in any particular group suffer collision without energy degradation till they have existed in that group for a time equal to the slowing down time for that energy interval, at the end of which they go over to the next group.

We shall divide the energy interval from source energy (which we shall throughout consider monoenergetic) to the thermal energy into $(n-1)$ groups, so that we have n groups including the thermal group. If L_k be the slowing down length, and t_k the slowing down time of the neutrons in

the group k, L_n the diffusion length and t_n the mean capture lifetime of thermal neutrons, then we have the following n differential equations for the n groups:

$$L_k^2 \nabla^2 \rho_k(\mathbf{r}, t) - \rho_k(\mathbf{r}, t) + \frac{t_k}{t_{k-1}} \rho_{k-1}(\mathbf{r}, t) = t_k \frac{\partial}{\partial t} \rho_k(\mathbf{r}, t) \qquad (1)$$

$$(k = 1, 2, 3, \ldots, n)$$

where $\rho_k(\mathbf{r}, t)$ is the density of the kth group neutrons at the point $\mathbf{r}$ and time t. $\rho_0(\mathbf{r}, t)$ is the source term and t_0 is taken to be unity. Writing $\rho_k(\mathbf{r}, t)/t_k = \phi_k(\mathbf{r}, t)$, we get for the thermal neutron distribution the equation

$$\prod_{k=1}^{n-1} \left(1 - L_k^2 \nabla^2 + t_k \frac{\partial}{\partial t}\right) \left[\left(1 - L_n^2 \nabla^2 + t_n \frac{\partial}{\partial t}\right) \phi_n(\mathbf{r}, t)\right] = \phi_0(\mathbf{r}, t) \qquad (2)$$

From (2) we get as the formal solution of the thermal neutron distribution as

$$\phi_n(\mathbf{r}, t) = \prod_{k=1}^{n-1} \left(1 - L_k^2 \nabla^2 + t_k \frac{\partial}{\partial t}\right)^{-1} \left(1 - L_n^2 \nabla^2 + t_n \frac{\partial}{\partial t}\right)^{-1} \phi_0(\mathbf{r}, t) \qquad (3)$$

We define $\prod_{k=1}^{n-1} \left(1 - L_k^2 \nabla^2 + t_k \frac{\partial}{\partial t}\right)^{-1}$ as the time-dependent n-group resolvant operator.

For the steady state we have instead of (1) the following n equations

$$L_k \nabla^2 \rho_k(\mathbf{r}) - \rho_k(\mathbf{r}) + \frac{t_k}{t_{k-1}} \rho_{k-1}(\mathbf{r}) = 0 \qquad (4)$$

$$(k = 1, 2, 3, \ldots, n)$$

which yields for the thermal neutron distribution

$$\prod_{k=1}^{n-1} (1 - L_k^2 \nabla^2) [(1 - L_n^2 \nabla^2) \phi_n(\mathbf{r})] = \phi_0(\mathbf{r}) \qquad (5)$$

Hence the formal solution for the thermal neutron distribution can be written as

$$\phi_n(\mathbf{r}) = \prod_{k=1}^{n-1} (1 - L_k^2 \nabla^2)^{-1} (1 - L_n^2 \nabla^2)^{-1} \phi_0(\mathbf{r})$$

$$= \left[\sum_{k=1}^{n} A_k (1 - L_k \nabla^2)\right] \phi_0(\mathbf{r}) \qquad (6)$$

where A_k is the coefficient of the kth term of the expansion of the continued products $\prod_{k=1}^{n}(1 - L_k^2 \lambda^2)^{-1}$ into partial fractions, where λ^2 is an algebraic variable. This expansion is possible since the operators $(1 - L_k^2 \nabla^2)$ $(k = 1, 2, \ldots, n)$ are commutative. Here $\prod_{k=1}^{n-1}(1 - L_k^2 \nabla^2)^{-1}$ is the n-group resolvant operator for the steady state.

Age Theory Approximation

In the age theory approximation we assume the energy loss of neutrons from source to thermal energy is a continuous process. This is equivalent to an infinite group theory. Hence the resolvant operators in the age theory approximation is obtained from the n-group resolvant operators by making $n \to \infty$. Then we get

(i) for steady state:

$$\lim_{n\to\infty} \left(\prod_{k=1}^{n-1} (1 - L_k^2 \nabla^2)^{-1} \right) \equiv e^{\tau_0 \nabla^2} \tag{7}$$

if the sequence $\sum_k L_k^2$ tends to the finite limit τ_0 when $k \to \infty$. Here τ_0 is the square of the mean slowing down length from source to thermal energy. It is called the 'age' of the source neutrons to thermal energy.

(ii) for time-dependent case:

$$\lim_{n\to\infty} \left(\prod_{k=1}^{n-1} \left[1 - L_k^2 \nabla^2 + t_k \frac{\partial}{\partial t} \right]^{-1} \right) \equiv e^{\tau_0 \nabla^2 - t_f \frac{\partial}{\partial t}} \tag{8}$$

if the sequence $\sum_k L_k^2 \to \tau_0$ as $k \to \infty$ and $\sum_k t_k \to t_f$ as $k \to \infty$.

Here τ_0 is same as in (7) and t_f is the mean slowing down time from source to thermal energy. Equation (8) could also be obtained from the age equation (see Appendix A).

The thermal neutron distribution in the age theory then becomes

$$\phi_n(\mathbf{r}) = e^{\tau_0 \nabla^2} (1 - L_n^2 \nabla^2)^{-1} \phi_0(\mathbf{r}) \tag{9}$$

for the steady state and

$$\phi_n(\mathbf{r}, t) = e^{\tau_0 \nabla^2 - t_f \frac{\partial}{\partial t}} \left(1 - L_n^2 \nabla^2 + t_n \frac{\partial}{\partial t} \right)^{-1} \phi_0(\mathbf{r}, t) \tag{10}$$

for the time-dependent state.

If $\phi_0(\mathbf{r}, t) = \Phi_0(\mathbf{r}) f(t)$, then

$$e^{\tau_0 \nabla^2 - t_f \frac{\partial}{\partial t}} \phi_0(\mathbf{r}, t) = e^{\tau_0 \nabla^2} \Phi_0(\mathbf{r}) e^{-t_f \frac{\partial}{\partial t}} f(t)$$

$$= e^{\tau_0 \nabla^2} \Phi_0(\mathbf{r}) \left\{1 - t_f \frac{\partial}{\partial t} + \frac{t_f^2}{2!} \frac{\partial^2}{\partial t^2} - \frac{\partial_f^3}{3!} \frac{\partial^3}{\partial t^3} + \ldots\right\} f(t)$$

$$= e^{\tau_0 \nabla^2} \Phi_0(\mathbf{r}) \left[f(t) - t_f f'(t) + \frac{t_f^2}{2!} f''(t) - \frac{t_f^3}{3!} f'''(t) + \cdot\cdot \right]$$

The expression inside the square bracket is the Taylor expansion of $f(t - t_f)$.

Therefore,

$$e^{\tau_0 \nabla^2 - t_f \frac{\partial}{\partial t}} \phi_0(\mathbf{r}, t) = e^{\tau_0 \nabla^2} \Phi_0(\mathbf{r}) f(t - t_f)$$

$$= e^{\tau_0 \nabla^2} \phi_0(\mathbf{r}, t - t_f) \tag{11}$$

Hence on the age theory the thermal neutron equivalent source is $e^{\tau_0 \nabla^2} \phi_0(\mathbf{r}, t - t_f)$ where t_f is the slowing down time. In the multigroup theory the neutrons in each group diffuse for a finite time equal to the slowing down time for that group before a transition to the next group takes place. Hence an initial burst of neutrons has a spread in time after each group and does not maintain the initial time characteristic. In the age theory these groups are infinitely small and hence the neutrons exist in any group only for an infinitely short time. So there is no diffusion in any group and hence the time characteristic is maintained throughout the fast region. We shall call this phenomenon time diffusion. Obviously the best approach is the multigroup theory with number of groups somewhere around the number of collisions. When the number of collisions is large, this would not differ very much from the age theory, but in the case of very light moderators like water, the continuous slowing down model is a poor approximation, since the number of collisions is small.

EXPLICIT SOLUTIONS FOR THERMAL NEUTRON DISTRIBUTION

The thermal neutron distribution is given by

$$\phi_n(\mathbf{r}, t) = \mathrm{F}\left(\nabla^2, \frac{\partial}{\partial t}\right) \phi_0(\mathbf{r}, t) \tag{12}$$

where $\mathrm{F}\left(\nabla^2, \frac{\partial}{\partial t}\right)$ is the appropriate 'diffusion' operator. The solution of (12) is obtained by expanding $\phi_n(\mathbf{r}, t)$ and $\phi_0(\mathbf{r}, t)$ into a series of

orthonormal functions $\lambda_\mu(\mathbf{r})\exp.(i\nu t)$ in r and t. Here $\lambda_\mu(\mathbf{r})$ are the eigenfunctions of the equation

$$\nabla^2\lambda_\mu(\mathbf{r}) + \omega^2{}_\mu\,\lambda_\mu(\mathbf{r}) = 0 \tag{13}$$

with the boundary condition that $\lambda_\mu(\mathbf{r})$ and all its spatial derivatives vanish on the boundary to which $\lambda_\mu(\mathbf{r})$ is defined. $\omega_\mu{}^2$ are the corresponding eigenvalues.

For a discrete eigenspectrum [this is the case when $\lambda_\mu(\mathbf{r})$ is defined within a finite boundary] we have

$$\phi_n(\mathbf{r}, t) = \sum_{\mu=0}^{\infty}\lambda_\mu(\mathbf{r})\int_{-\infty}^{+\infty}\mathrm{B}_\mu(\nu)\,e^{i\nu t}\,d\nu$$

$$\phi_0(\mathbf{r}, t) = \sum_{\mu=0}^{\infty}\lambda_\mu(\mathbf{r})\int_{-\infty}^{+\infty}\mathrm{A}_\mu(\nu)\,e^{i\nu t}\,d\nu \tag{14}$$

Here $\mathrm{A}_\mu(\nu)$ and $\mathrm{B}_\mu(\nu)$ are the coefficients of the expansion. $\mathrm{A}_\mu(\nu)$ can be determined from the nature of the source term $\phi_0(\mathbf{r}, t)$. Substituting (14) in (12) we get

$$\sum_{\mu=0}^{\infty}\lambda_\mu(\mathbf{r})\int_{-\infty}^{+\infty}\mathrm{B}_\mu(\nu)\,e^{i\nu t}\,d\nu = \mathrm{F}\left(\nabla^2, \frac{\partial}{\partial t}\right)\sum_{\mu=0}^{\infty}\lambda_\mu(\mathbf{r})\int_{-\infty}^{+\infty}\mathrm{A}_\mu(\nu)\,e^{i\nu t}d\nu. \tag{15}$$

From the orthonormal properties of $\lambda_\mu(\mathbf{r})$ we have, since

$$\mathrm{F}\left(\nabla^2, \frac{\partial}{\partial t}\right)\lambda_\mu(r)\,e^{i\nu t} = \mathrm{F}(-\omega_\mu{}^2, i\nu)\,\lambda_\mu(\mathbf{r})\,e^{i\nu t}$$

$$\mathrm{B}_\mu(\nu) = \mathrm{F}(-\omega_\mu{}^2, i\nu)\,\mathrm{A}_\mu(\nu) \tag{16}$$

Hence

$$\phi_n(\mathbf{r}, t) = \sum_{\mu=0}^{\infty}\lambda_\mu(\mathbf{r})\int_{-\infty}^{+\infty}\mathrm{A}_\mu(\nu)\,\mathrm{F}(-\omega_\mu{}^2, i\nu)\,e^{i\nu t}\,d\nu \tag{17}$$

This completes the formal solution for finite boundaries.

When the eigenspectrum is continuous, the summation is replaced by integration. Let k^2 be the continuous eigenspectrum of the equation

$$\nabla^2\lambda(\mathbf{k}, \mathbf{r}) + k^2\lambda(\mathbf{k}, \mathbf{r}) = 0.$$

Then $\lambda(\mathbf{k}, \mathbf{r})$ is a plane wave $\exp.(i\mathbf{k}.\mathbf{r})$. Hence we get

$$\mathrm{F}\left(\nabla^2, \frac{\partial}{\partial t}\right)\lambda(\mathbf{k}, \mathbf{r})\,e^{i\nu t} = \mathrm{F}(-k^2, i\nu)\,e^{i\mathbf{k}.\mathbf{r}}\,e^{i\nu t} \tag{18}$$

so that

$$B(k, \nu) = F(-k^2, i\nu)\, A(\mathbf{k}, \nu)$$

Therefore the thermal neutron distribution is given by

$$\phi_n(\mathbf{r}, t) = \int_{(k)} e^{i\mathbf{k}.\mathbf{r}}\, d\mathbf{k} \int_{-\infty}^{+\infty} A(\mathbf{k}, \nu)\, F(-k^2, i\nu)\, e^{i\nu t}\, d\nu \tag{19}$$

This completes the solution for continuous eigenspectrum (*i.e.*, infinite boundary).

We shall now evaluate (17) and (19) on age and twogroup approximations for a finite as well as for an infinite geometry. We shall consider an instantaneous point source of fast neutrons as well as a point source of finite width in time.

For an instantaneous point source we have

$$\phi_0(\mathbf{r}, t) = \phi_0 \delta(\mathbf{r})\, \delta(t) \tag{20}$$

where ϕ_0 is the source strength. Then

$$A(\mathbf{k}, \nu) = A(\mathbf{k})/2\pi = 1/16\pi^4 \tag{21}$$

$$A_\mu(\nu) = A_\mu/2\pi \tag{22}$$

For a rectangular parallelopiped of sides a, b, c, origin at one of the corners and source at (x', y', z')

$$A_\mu = A_{lmn} = \frac{8\phi_0}{abc} \sin\frac{l\pi x'}{a} \sin\frac{m\pi y'}{b} \sin\frac{n\pi z'}{c}$$

$$\lambda_\mu(\mathbf{r}) = \lambda_{lmn}(x, y, z) = \sin\frac{l\pi x}{a} \sin\frac{m\pi y}{b} \sin\frac{n\pi z}{c}$$

$$\omega_\mu^2 = \omega_{lmn}^2 = \pi^2\left[\frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2}\right] \tag{23}$$

For a point source of finite width in time we have

$$\phi_0(\mathbf{r}, t) = \phi_0 \delta(\mathbf{r})\, [I(t) - I(t - \triangle t)] \tag{24}$$

where $I(t)$ is the Heaveside unit step function. Then

$$A_\mu(\nu) = \frac{A_\mu}{2\pi} \int_0^{\triangle t} e^{i\nu x}\, dx \tag{25}$$

$$A(\mathbf{k}, \nu) = \frac{1}{16\pi^4} \int_0^{\triangle t} e^{i\nu x}\, dx \tag{26}$$

I. *The Age Theory Approximation*

The diffusion operator is given by

$$F\left(\nabla^2,\ \frac{\partial}{\partial t}\right) = e^{\tau_0 \nabla^2 - t_f \frac{\partial}{\partial t}} \left(1 - L_n^2\ \nabla^2 + t_n \frac{\partial}{\partial t}\right)^{-1}$$

I.1 *Finite Geometry*

(*a*) Instantaneous source

$$\phi_n(r, t) = \frac{1}{2\pi} \sum_{\mu=0}^{\infty} A_\mu\, \lambda_\mu(r) \int_{-\infty}^{+\infty} \frac{e^{-\tau_0 \omega_\mu^2 - i\nu t_f}\ e^{i\nu t}}{(1 + \omega_\mu^2\, L_n^2 + i\nu t_n)}\, d\nu$$

$$= \frac{1}{t_n} \sum_{\mu=0}^{\infty} I(t - t_f)\, A_\mu\, \lambda_\mu(r)\, e^{-\tau_0 \omega \mu^2}\ e^{-\frac{1 + \omega_\mu^2 L_n^2}{t_n}(t - t_f)} \tag{27}$$

where $I(t - t_f)$ is the Heaveside unit step function.

(*b*) $\triangle t$ source:

$$\phi_n(r, t) = \sum_{\mu} \lambda_\mu(r) \int_{-\infty}^{+\infty} \frac{A_\mu(\nu)\ e^{-\tau_0 \omega \mu^2}\ e^{i\nu t}\ e^{-i\nu t_f}}{(1 + \omega_\mu^2 L_n^2 + i\nu t_n)}\, d\nu$$

$$= \frac{1}{2\pi} \sum_{\mu} A_\mu\, e^{-\tau_0 \omega \mu^2}\, \lambda_\mu(r) \int_0^{\triangle t} dx \int_{-\infty}^{+\infty} \frac{e^{i\nu(t - t_f - x)}}{(1 + \omega_\mu^2\, L_n^2 + i\nu t_n)}\, d\nu$$

$$= \sum_{\mu} I(t - t_f)\, A_\mu\, \lambda_\mu(r)\, e^{-\tau_0 \omega \mu^2}\ \frac{1 - e^{-\frac{1 + \omega_\mu^2 L_n^2}{t_n}(t - t_f)}}{1 + \omega_\mu^2\, L_n^2} \qquad (0 < t < \triangle t)$$

$$= \sum_{\mu} I(t - t_f)\, A_\mu\, \lambda_\mu(r)\, e^{-\tau_0 \omega \mu^2}\, e^{-\frac{1 + \omega_\mu^2 L_n^2}{t_n}(t - t_f)} \left(e^{\frac{1 + \omega_\mu^2 L_n^2}{t_n} \triangle t} - 1\right) \qquad (t > \triangle t) \tag{28}$$

I.2. *Infinite Geometry*

(*a*) Instantaneous source:

$$\phi_n(r, t) = \int_{(k)} e^{i\mathbf{k}.\mathbf{r}}\, d\mathbf{k} \int_{-\infty}^{+\infty} A(\mathbf{k}, \nu)\, \frac{e^{-\tau_0 k^2 - i\nu t_f}\ e^{i\nu t}}{(1 + k^2\, L_n^2 + i\nu t_n)}\, d\nu$$

$$= \frac{\phi_0}{8\pi^3 t_n} \int_{(k)} e^{i\mathbf{k}.\mathbf{r}}\ e^{-\tau_0 k^2}\, e^{-\frac{1 + k^2 L_n^2}{t_n}(t - t_f)}\ I(t - t_f)\, d\mathbf{k}$$

$$= \frac{e^{-(t-t_f)/t_n}\ \phi_0\, \mathrm{I}(t-t_f)}{2\pi^2 r t_n} \int_0^\infty k^{3/2}\, r^{\frac{1}{2}}\ e^{-\left[\tau_0 + \frac{\mathrm{L}_n^2 (t-t_f)}{t_n}\right] k^2} \frac{\sin kr}{\sqrt{kr}}\, dk$$

$$= \frac{\phi_0\, e^{-(t-t_f)/t_n}\, \mathrm{I}(t-t_f)}{\pi^{3/2} t_n} \text{ Exp.} \left\{ - \frac{r^2}{4\left[\tau_0 + \frac{\mathrm{L}_n^2 (t-t_f)}{t_n}\right]} \right\}$$

$$\times \left[4\left(\tau_0 + \frac{\mathrm{L}_n^2 (t-t_f)}{t_n}\right)\right]^{-3/2} \qquad (29)$$

(*b*) $\triangle t$ source:

$$\phi_n(r, t) = \frac{1}{16\pi^4} \int_{(k)} e^{i\mathbf{k}.\mathbf{r}}\ e^{-\tau_0 k^2}\, d\mathbf{k} \int_0^{\triangle t} dx \int_{-\infty}^{+\infty} \frac{e^{iv\,(t^*-x)}}{(1 + k^2 \mathrm{L}_n^2 + ivt_n)}\, dv$$

$$= \frac{1}{8\pi^3 t_n} \int_{(k)} e^{i\mathbf{k}.\mathbf{r}}\ e^{-\tau_0 k^2}\, d\mathbf{k} \int_0^{\triangle t} \mathrm{I}(t^* - x)\, e^{-\frac{1 + k^2 \mathrm{L}_n^2}{t_n}(t^* - x)}\, dx$$

$$= \frac{1}{8\pi^3} \int_{(k)} \frac{e^{-\tau_0 k^2}\ e^{i\mathbf{k}.\mathbf{r}}}{1 + k^2 \mathrm{L}_n^2} \left[1 - e^{-\left(\frac{1 + k^2 \mathrm{L}_n^2}{t_n}\right) t^*}\right] \mathrm{I}(t^*)\, d\mathbf{k} \qquad (0 < t < \triangle t)$$

$$= \frac{1}{8\pi^3} \int_{(k)} \frac{e^{-\tau_0 k^2}\ e^{i\mathbf{k}.\mathbf{r}}}{1 + k^2 \mathrm{L}_n^2} \left[e^{\left(\frac{1 + k^2 \mathrm{L}_n^2}{t_n}\right) \triangle t} - 1\right] e^{-\left(\frac{1 + k^2 \mathrm{L}_n^2}{t_n}\right) t^*} \mathrm{I}(t^*)\, d\mathbf{k} \qquad (30)$$

where $t^* = t - t_f$.

Now

$$\int_{(k)} \frac{e^{i\mathbf{k}.\mathbf{r}}\ e^{-ak^2}}{1 + k^2 \mathrm{L}_n^2}\, dk = 2\pi \int_0^\infty \frac{k^2\, e^{-ak^2}}{1 + k^2 \mathrm{L}_n^2}\, dk \int_{-1}^{+1} e^{ikr\mu}\ d\mu$$

$$= \frac{4\pi}{r} \int_0^\infty \frac{k e^{-ak^2} \operatorname{Sin} kr}{1 + k^2 \mathrm{L}_n^2}\, dk = \frac{4\pi}{r}\, \mathrm{I}(a, \mathrm{L}_n)$$

where $\mathrm{I}(a, \mathrm{L}_n)$ has been shown in the appendix to be

$$\mathrm{I}(a, \mathrm{L}_n) = \frac{\pi}{4r\mathrm{L}_n^2}\ e^{a/\mathrm{L}_n^2} \left[e^{-r/\mathrm{L}_n} \left\{1 - erf\left(\frac{\sqrt{a}}{\mathrm{L}_n} - \frac{r}{2\sqrt{a}}\right)\right\} \right.$$

$$\left. - e^{\ r/\mathrm{L}_n} \left\{1 - erf\left(\frac{\sqrt{a}}{\mathrm{L}_n} + \frac{r}{2\sqrt{a}}\right)\right\}\right] \qquad (31)$$

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\, du$$

Hence (30) becomes

$$\phi_n(\mathbf{r}, t) = \frac{\phi_0 \, I(t^*)}{2\pi^2 r}\left[I(\tau_0, L_n) - e^{-t^*/t_n} \, I(a, L_n)\right]$$

$$(0 < t < \triangle t)$$

$$= \frac{\phi_0 \, I(t^*)}{2\pi^2 r}\left[e^{-t'^*/t_n} \, I(\tau_0, L_n) - e^{-t^*/t_n} \, I(a, L_n)\right] (t > \triangle t) \qquad (32)$$

where

$$a = \tau_0 + \frac{L_n^2 (t - t_f)}{t_n} \; ; \; a' = \tau_0 + \frac{L_n^2 (t - t_f - \triangle t)}{t_n}$$

$$t^* = (t - t_f); \; t'^* = (t - t_f - \triangle t).$$

II. *Two Group Theory*

The diffusion operator is given by

$$F\left(\nabla^2, \frac{\partial}{\partial t}\right) = \left(1 - L_f^2 \nabla^2 + t_f \frac{\partial}{\partial t}\right)^{-1} \left(1 - L_n^2 \nabla^2 + t_n \frac{\partial}{\partial t}\right)^{-1}$$

where $L_f^2 = \tau_0$, the ' age ' and t_f is the mean slowing down time in the fast group.

II.1. *Finite Geometry*

(*a*) Instantaneous point source:

$$\phi_n(r, t) = \frac{1}{2\pi} \sum_\mu A_\mu \lambda_\mu(r) \int_{-\infty}^{+\infty} \frac{e^{i\nu t}}{(1 + \omega_\mu^2 L_f^2 + i\nu t_f)(1 + \omega_\mu^2 L_n^2 + i\nu t_n)} \, d\nu$$

$$= \sum_\mu \frac{A_\mu \lambda_\mu(r)}{t_n t_f}\left[\frac{e^{-\Phi_\mu^n t} - e^{-\Phi_\mu^f t}}{\Phi_\mu^n - \Phi_\mu^f}\right] \qquad (33)$$

Where

$$\Phi_\mu^f = \frac{1 + \omega_\mu^2 L_f^2}{t_f} \; ; \; \Phi_\mu^n = \frac{1 + \omega_\mu^2 L_n^2}{t_n}$$

(*b*) $\triangle t$ source:

$$\phi_n(r, t) = \frac{1}{2\pi} \sum_\mu A_\mu \lambda_\mu(r) \int_{-\infty}^{+\infty} d\nu \int_0^{\triangle t} e^{i\nu x} dx \frac{e^{i\nu t}}{(1 + \omega_\mu^2 L_n^2 + i\nu t_n)(1 + \omega_\mu^2 L_f^2 + i\nu t_f)}$$

$$= \frac{1}{2\pi} \sum_\mu A_\mu \lambda_\mu(r) \int_0^{\triangle t} dx \int_{-\infty}^{+\infty} \frac{e^{i\nu(t-x)}}{[1 + \omega_\mu^2 L_n^2 + i\nu t_n][1 + \omega_\mu^2 L_f^2 + i\nu t_f]} \, d\nu$$

$$= \sum_{\mu} \frac{A_\mu \lambda_\mu (r)}{- t_n t_f} \int_0^{\triangle t} I(t-x) \frac{e^{-\Phi_\mu{}^n (t-x)} - e^{-\Phi_\mu{}^f (t-x)}}{[\Phi_\mu{}^n - \Phi_\mu{}^f]} dx$$

$$= \sum_{\mu} \frac{A_\mu \lambda_\mu (r)}{t_n t_f (\Phi_\mu{}^n - \Phi_\mu{}^f)} \left[\frac{1 - e^{-\Phi_\mu{}^f t}}{\Phi_\mu{}^f} - \frac{1 - e^{-\Phi_\mu{}^n t}}{\Phi_\mu{}^n} \right] (0 < t < \triangle t)$$

$$= \sum_{\mu} \frac{A_\mu \lambda_\mu (r)}{t_n t_f (\Phi_\mu{}^n - \Phi_\mu{}^f)} \left[\frac{e^{-\Phi_\mu{}^f t'} - e^{-\Phi_\mu{}^f t}}{\Phi_\mu{}^f} - \frac{e^{-\Phi_\mu{}^n t'} - e^{-\Phi_\mu{}^n t}}{\Phi_\mu{}^n} \right]$$

$$(t > \triangle t) \qquad .(34)$$

where $\Phi_\mu{}^{n,f}$ are same in (33) and $t' = t - \triangle t$.

II.2. *Infinite Geometry*

(*a*) Instantaneous Source:

$$\phi_n (r, t) = \frac{\phi_0}{16\pi^4} \int_{(k)} e^{i\mathbf{k}.\mathbf{r}} \, d\mathbf{k} \int_{-\infty}^{+\infty} \frac{e^{i\nu t}}{(1+k^2 L_n{}^2 + i\nu t_n)(1+k^2 L_f{}^2 + i\nu t_f)} \, d\nu$$

$$= \frac{1}{8\pi^3} \int_{(k)} e^{i\mathbf{k}.\mathbf{r}} \left[\frac{e^{-\frac{1+k^2 L_f{}^2}{t_f} t} - e^{-\frac{1+k^2 L_n{}^2}{t_n} t}}{t_f (1 + k^2 L_n{}^2) - t_n (1+k^2 L_f{}^2)} \right] d\mathbf{k}$$

$$= \frac{1}{8\pi^3} \left[e^{-t/t_f} \int_{(k)} \frac{e^{i\mathbf{k}.\mathbf{r}} \, e^{-\alpha_f k^2}}{1 + \mu k^2} \, d\mathbf{k} - e^{-t/t_n} \int_{(k)} \frac{e^{i\mathbf{k}.\mathbf{r}} \, e^{-\alpha_n k^2}}{1 + \mu k^2} \, d\mathbf{k} \right]$$

$$= \frac{1}{2\pi^2 \beta r} \left[e^{-t/t_f} I(\alpha_f, \sqrt{\mu}) - e^{-t/t_n} I(\alpha_n, \sqrt{\mu}) \right] \qquad (35)$$

where

$$\alpha_n = \frac{L_n{}^2 t}{t_n} \qquad \alpha_f = \frac{L_f{}^2 t}{t_f}$$

$$\beta = t_f - t_n \qquad \mu = \frac{L_n{}^2 t_f - L_f{}^2 t_n}{\beta}$$

(*b*) $\triangle t$ Source:

$$\phi_n (r, t) = \frac{1}{16\pi^4} \int_{(k)} e^{i\mathbf{k}.\mathbf{r}} \, d\mathbf{k} \int_0^{\triangle t} dx \int_{-\infty}^{+\infty} \frac{e^{i\nu(t-x)}}{(1+k^2 L_n{}^2 + i\nu t_n)(1+k^2 L_f{}^2 + i\nu t_f)} \, d\nu$$

$$= \frac{1}{8\pi^3} \int_{(k)} \frac{e^{i\mathbf{k}.\mathbf{r}}}{t_n t_f} \, d\mathbf{k} \int_0^{\triangle t} I(t-x) \left[\frac{e^{-\frac{1+k^2 L_f{}^2}{t_f}(t-x)} - e^{-\frac{1+k^2 L_n{}^2}{t_n}(t-x)}}{\left(\frac{1+k^2 L_n{}^2}{t_n}\right) - \left(\frac{1+k^2 L_f{}^2}{t_f}\right)} \right] dx$$

for $0 < t < \triangle t$

$$\phi_n(\mathbf{r}, t) = \frac{1}{8\pi^3}\Bigg[\int_{(k)} t_f e^{i\mathbf{k}.\mathbf{r}}\ e^{-t/t_f}\ e^{-a_f k^2}\ \frac{\left[e^{\frac{1+k^2L_f^2}{t_f}t} - 1\right]}{(\beta + \lambda k^2)(1 + k^2 L_f{}^2)}\, d\mathbf{k}$$

$$- \int_{(k)} t_n\ e^{i\mathbf{k}.\mathbf{r}}\ e^{-t/t_n}\, e^{-a_n k^2}\ \frac{\left[e^{\frac{1+k^2L_n^2}{t_n}t} - 1\right]}{(\beta + \lambda k^2)(1 + k^2 L_n{}^2)}\, d\mathbf{k}\Bigg]$$

$$= \frac{1}{2\pi^2 \beta r}\Big[\mathrm{I}(0, \sqrt{\mu})\Big\{t_n \frac{\mu}{\mu_n - \mu} - t_f \frac{\mu}{\mu_f - \mu}\Big\}$$

$$- \mathrm{I}(0, \sqrt{\mu_n})\, t_n \frac{\mu_n}{\mu_n - \mu} + \mathrm{I}(0, \sqrt{\mu_f})\, t_f \frac{\mu_f}{\mu_f - \mu}$$

$$- \mathrm{I}(a_n, \sqrt{\mu})\, t_n \frac{\mu e^{-t/t_n}}{\mu_n - \mu} + \mathrm{I}(a_f, \sqrt{\mu})\, t_f \frac{\mu e^{-t/t_f}}{\mu_f - \mu}$$

$$+ \mathrm{I}(a_n, \sqrt{\mu_n})\, t_n \frac{\mu_n e^{-t/t_n}}{\mu_n - \mu} - \mathrm{I}(a_f, \sqrt{\mu_f})\ \frac{\mu_f e^{-t/t_f}}{\mu_f - \mu}\Big] \qquad (36)$$

for $t > \triangle t$

$$\phi_n(r, t) = \frac{1}{8\pi^3 \beta} \int_{(k)} \frac{e^{ik\cdot r}}{(1 + \mu k^2)} \left[\frac{t_f}{1 + k^2 L_f{}^2} e^{-\frac{1+k^2L_f^2}{t_f}t}\left(e^{\frac{1+k^2L_f^2}{t_f}\triangle t} - 1\right)\right.$$

$$\left. - \frac{t_n}{1 + k^2 L_n{}^2} e^{-\frac{1+k^2L_n^2}{t_n}t}\left(e^{\frac{1+k^2L_n^2}{t_n}\triangle t} - 1\right)\right] dk$$

$$= \frac{1}{2\pi^2 r \beta}\Big[t_n \frac{\mu e^{-t'/t_n}}{\mu_n - \mu}\, \mathrm{I}(a_n', \sqrt{\mu}) - t_f \frac{\mu e^{-t'/t_f}}{\mu_f - \mu}\, \mathrm{I}(a_f', \sqrt{\mu})$$

$$- t_n \frac{\mu_n}{\mu_n - \mu} e^{-t'/t_n}\, \mathrm{I}(a_n', \sqrt{\mu_n}) + t_f \frac{\mu_f}{\mu_f - \mu} e^{-t/t_f}\, \mathrm{I}(a_f', \sqrt{\mu_f})$$

$$- t_n \frac{\mu e^{-t/t_n}}{\mu_n - \mu}\, \mathrm{I}(a_n, \sqrt{\mu}) + t_f \frac{\mu}{\mu_f - \mu} e^{-t/t_f}\, \mathrm{I}(a_f, \sqrt{\mu})$$

$$+ t_n \frac{\mu_n}{\mu_n - \mu}\ e^{-t/t_n}\, \mathrm{I}(a_n, \sqrt{\mu_n}) - t_f \frac{\mu_f}{\mu_f - \mu}\ e^{-t/t_f}\, \mathrm{I}(a_f, \sqrt{\mu_f})\Big] \qquad (37)$$

where

$$a_n = L_n{}^2 t/t_n \qquad a_n' = L_n{}^2\, t'/t_n \qquad t' = t - \triangle t$$

$$a_f = L_f{}^2 t/t_f \qquad a_f' = L_f{}^2 t'/t_f$$

$$\mu_n = L_n{}^2 \qquad \beta = t_f - t_n$$

$$\mu_f = L_f{}^2 \qquad \mu = (L_n{}^2 t_f - L_f{}^2 t_n)/\beta \qquad \lambda = \mu\beta$$

DISCUSSION

In the case of finite geometries, the absolute neutron density at any point in space at any instance, is larger on the two group approximation than on the age approximation; for, on the age theory, the non-leakage term for fast neutrons is exp. $[-\tau_0\omega_\mu{}^2]$ whereas on the two group theory it is $(1+\tau_0\omega_\mu{}^2)^{-1}$. However, as the size of the moderator decreases, exp. $(-\tau_0\omega_\mu{}^2)$ approaches $(1+\tau_0\omega_\mu{}^2)^{-1}$ and hence there is better agreement between the two theories.

In the case of ordinary water, the age and two group approximations have been applied for infinite geometries. The agreement of these results has been compared with experimental data by Ramanna *et al.*[2]

We are grateful to Dr. R. Ramanna for suggesting the problem and for helpful discussions throughout the course of the work. We also thank Mr. Udgonkar for many helpful discussions.

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APPENDIX A

Symbolic Solution of the Time-Dependent 'Age' Equation

Consider the balance of neutrons of energy between E and E + dE. We get

$$D \nabla^2 n(\mathbf{r}, t, E)\, dE + \frac{\partial}{\partial E} [\chi(\mathbf{r}, t, E)]\, dE = \frac{\partial}{\partial t} n(\mathbf{r}, t, E)\, dE, \tag{1}$$

where

$n(\mathbf{r}, t, E)\, dE$ is the density of neutrons of energy between E and E + dE at the position $\mathbf{r}$ and at time t.

$\chi(\mathbf{r}, t, E)\, dE$ is the slowing down density of neutrons at energy E at the position $\mathbf{r}$ and at time t

and

D is the diffusion coefficient of the medium for neutrons of energy E. The following relations hold

$$n(\mathbf{r}, t, E)\, dE = \frac{\lambda_s}{\xi \nu E} \chi(\mathbf{r}, t, E)\, dE;\ D = \lambda_t \nu/3. \tag{2}$$

where

λ_s = scattering mean free path for neutrons of energy E in the medium.

λ_t = transport mean free path.

ν = velocity of neutrons of energy E.

ξ = average logarithmic loss of energy.

Substituting in (1)

$$\frac{\lambda_s \lambda_t}{3\xi E} \nabla^2 \chi + \frac{\partial \chi}{\partial E} = \frac{\lambda_s}{\xi \nu E} \frac{\partial \chi}{\partial t} \tag{3}$$

Introduce a new variable τ_0 called age defined by

$$\tau_0 = \frac{1}{3\xi} \int_E^{E_0} \lambda_s(E)\, \lambda_t(E)\, \frac{dE}{E} \tag{4}$$

from (3)

$$\frac{\lambda_s \lambda_t}{3\xi E} \nabla^2 \chi - \frac{\lambda_s \lambda_t}{3\xi E} \frac{\partial \chi}{\partial \tau_0} = \frac{\lambda_s}{\xi \nu E} \frac{\partial \chi}{\partial E}$$

or

$$\nabla^2 \chi(\mathbf{r}, t, \tau_0) - \frac{\partial}{\partial \tau_0}[\chi(\mathbf{r}, t, \tau_0)] = \frac{1}{D(\tau_0)} \frac{\partial}{\partial t}[\chi(\mathbf{r}, t, \tau_0)]. \quad (5)$$

This is the time-dependent age equation.

Let $\chi(r, t, o) = \phi_0(r, t)$

where $\phi_0(\mathbf{r}, t)$ can be expanded into orthonormal eigenfunctions under appropriate boundary conditions as previously described in the text.

Then the solution is

$$\chi(\mathbf{r}, t, \tau_0) = \exp\left\{\left[\int_0^{\tau_0} d\tau_0\right]\nabla^2 - \left[\int_0^{\tau_0} \frac{1}{D(\tau_0)}\, d\tau_0\right]\frac{\partial}{\partial t}\right\}\phi(\mathbf{r}, t)$$

from (4) we can get

$\tau_0 = \int_0^{t_f} D\ dt$ where t_f is the slowing down time for a neutron of age τ_0.

$$\text{Then} \quad \int_0^{\tau_0} \frac{1}{D(\tau_0)}\, d\tau_0 = \int_0^{t_f} dt = t_f\,; \quad \int_0^{\tau_0} d\tau_0 = \tau_0.$$

$$\text{So,} \qquad \chi(\mathbf{r}, t, \tau_0) = \exp\left[\tau_0 \nabla^2 - t_f \frac{\partial}{\partial t}\right]\phi_0(\mathbf{r}, t)$$

APPENDIX B

Evaluation of the Integral $I(\mu, \nu)$

$$I(\mu, \nu) = \int_0^\infty k \frac{e^{-\mu k^2} \sin kr}{1 + k^2\nu^2} \, dk$$

$$= \int_0^\infty k e^{-\mu k^2} \sin kr \left[\int_0^\infty e^{-x(1+\nu^2 k^2)} dx \right] dk$$

$$= \int_0^\infty e^{-x} \, dx \int_0^\infty k e^{-(\mu+\nu^2 x)k^2} \sin kr \, dk$$

$$= r^{\frac{1}{2}} \int_0^\infty e^{-x} \, dx \int_0^\infty k^{3/2} e^{-(\mu+\nu^2 x)k^2} J_{\frac{1}{2}}(kr) \, dk$$

$$= \frac{\sqrt{\pi}}{4} \int_0^\infty e^{-x} \frac{e^{-r^2/[4(\mu+\nu^2 x)]}}{(\nu^2 x + \mu)^{3/2}} \, dx$$

Let $t = r/2(\mu + \nu^2 x)^{\frac{1}{2}}$; when $\begin{cases} x = 0 & t = r/2\sqrt{\mu} \\ x = \infty & t = 0 \end{cases}$

Since x varies from 0 to ∞, x is positive. Similarly t is positive since it varies from 0 to $r/2\sqrt{\mu}$, r and $\sqrt{\mu}$ being positive as they are physical constants.

$$\therefore \quad I(\mu, \nu) = e^{\mu/\nu^2} \frac{\sqrt{\pi}}{r\nu^2} \int_0^{r/2\sqrt{\mu}} \exp\left[-\left(\frac{r^2}{4t^2\nu^2} + t^2 \right) \right] dt$$

$$= \frac{\sqrt{\pi}}{2r\nu^2} e^{\mu/\nu^2} \left[e^{-r/\nu} \int_0^{r/2\sqrt{\mu}} \exp\left[-\left(\frac{r}{2t\nu} - t \right)^2 \right] dt + e^{r/\nu} \int_0^{r/2\sqrt{\mu}} \exp\left[-\left(\frac{r}{2t\nu} + t \right)^2 \right] dt \right]$$

$$= \frac{\sqrt{\pi}}{2r\nu^2} e^{\mu/\nu^2} \left[e^{-r/\nu} I_- + e^{+r/\nu} I_+ \right]$$

where

$$I_\pm = \int_0^{r/2\sqrt{\mu}} \exp\left[-\left(\frac{r}{2t\nu} \pm t \right)^2 \right] dt$$

Consider the integral I

Let $$\left(\frac{r}{2t\nu} - t\right) = u.$$

$$t = \frac{-u \pm \sqrt{u^2 + 2r/\nu}}{2}.$$

If u is negative, then we can define $u' = (t - r/2t\nu)$

so that

$$t = \frac{u' \pm \sqrt{u'^2 + 2r/\nu}}{2}$$

since t is always + ve and since $\sqrt{u^2 + 2r/\nu} > u$ and $\sqrt{u'^2 + 2r/\nu} > u'$ in both cases, the positive sign must be used.

The limits of integration are given by

$$t = 0 \to u = \infty \text{ and } t = \frac{r}{2\sqrt{\mu}} \to u = \frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}$$

$$\therefore \quad \mathrm{L} = \int_0^{r/2\sqrt{\mu}} \exp\left[-\left(\frac{r}{2t\nu} - t\right)^2\right] dt$$

$$= -\tfrac{1}{2}\int_{\infty}^{\left(\frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}\right)} e^{-u^2}\, du + \tfrac{1}{2}\int_{\infty}^{\left(\frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}\right)} e^{-u^2} \frac{udu}{\sqrt{u^2 + 2r/\nu}}$$

Now

$$\int_{\infty}^{\left(\frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}\right)} e^{-u^2} \frac{udu}{\sqrt{u^2 + 2r/\nu}} = e^{2r/\nu} \int_{\infty}^{\left(\frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}\right)} \frac{e^{-(u^2 + 2r/\nu)}}{\sqrt{u^2 + 2r/\nu}} udu.$$

Let $$u^2 + \frac{2r}{\nu} = y^2.$$

Then

$$\int_{\infty}^{\left(\frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}\right)} e^{-u^2} \frac{udu}{\sqrt{u^2 + 2r/\nu}} = e^{2r/\nu} \int_{\infty}^{\left(\frac{\sqrt{\mu}}{\nu} + \frac{r}{2\sqrt{\mu}}\right)} e^{-y^2}\, dy,$$

$$\therefore \mathrm{L} = \tfrac{1}{2}\int_{\left(\frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}\right)}^{\infty} e^{-u^2}\,du - \frac{e^{2\tau/\nu}}{2}\int_{\left(\frac{\sqrt{\mu}}{\nu} + \frac{r}{2\sqrt{\mu}}\right)}^{\infty} e^{-u^2}\,du,$$

$$= \frac{\sqrt{\pi}}{4}\left[1 - erf\left(\frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}\right)\right] - \frac{\sqrt{\pi}}{4}\,e^{2\tau/\nu}\left[1 - erf\left(\frac{\sqrt{\mu}}{\nu} + \frac{r}{2\sqrt{\mu}}\right)\right]$$

Similarly it can be shown that

$$\mathrm{L}_{+} = \frac{\sqrt{\mu}}{4}\,e^{-2\tau/\nu}\left[1 - erf\left(\frac{\sqrt{\mu}}{\nu} - \frac{\nu}{2\sqrt{\mu}}\right)\right] - \frac{\sqrt{\pi}}{4}\left[1 - erf\left(\frac{\sqrt{\mu}}{\nu} + \frac{r}{2\sqrt{\mu}}\right)\right]$$

$$\therefore \quad \mathrm{I}(\mu, \nu) = \frac{\sqrt{\pi}}{2r\nu^2}\,e^{\mu/\nu^2}\left[e^{-\tau/\nu}\,\mathrm{L} + e^{\tau/\nu}\,\mathrm{L}_{+}\right]$$

$$= \frac{\pi}{4r\nu^2}\,e^{\mu/\nu^2}\left[e^{-\tau/\nu}\left\{1 - erf\left(\frac{\sqrt{\mu}}{\nu} - \frac{r}{2\sqrt{\mu}}\right)\right\}\right.$$

$$\left. - e^{\tau/\nu}\left\{1 - erf\left(\frac{\sqrt{\mu}}{\nu} + \frac{r}{2\sqrt{\mu}}\right)\right\}\right]$$

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part LV. A New Synthesis of 7-Hydroxy-Chromeno-(3′ : 4′ : 2 : 3)-Chromone

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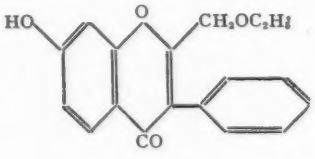
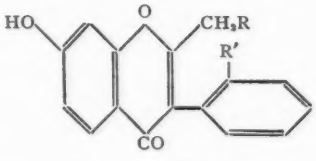
In an earlier publication[1] a general method for the synthesis of the four ringed chromeno-chromone unit of the rotenoid skeleton was described based on considerations of possible biogenesis from the related 2-methyl isoflavone. There were a number of stages in this synthesis and the yields were poor. Successful attempts have now been made to simplify the synthesis of such compounds in order to make them available in good yields for further synthetic work.

The new method is based on the earlier findings of La Forge,[2] Baker and co-workers,[3] and Mehta and Seshadri[4] that acid chlorides can be made to condense with desoxy benzoins in presence of pyridine to yield isoflavones. Ethoxy acetyl chloride[5] has now been used as the appropriate reagent. A pilot experiment using ω-phenyl resacetophenone[6] gave a good yield of 2-ethoxymethyl-7-hydroxy isoflavone (I) which on treatment with hydrobromic acid-glacial acetic acid mixture is converted into the 2-bromomethyl derivative which has been reported earlier.[7] When 2 : 4-dihydroxy-2′-methoxy phenyl benzyl ketone[1] is used, 2-bromo-methyl-7 : 2′-dihydroxy isoflavone (II *b*) is obtained through the intermediate (II *a*). It has been

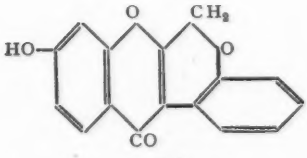


I



II

(*a*) R = OC_2H_5 ; R′ = OCH_3
(*b*) R = Br; R′ = HO



III

found during this work that treatment of 2-ethoxy methyl isoflavones with hydrobromic acid at higher temperature results in considerable resin formation and good results are obtained by employing mild conditions as described in the experimental part. The bromo-methyl-dihydroxy isoflavone (II *b*) readily eliminates a molecule of hydrogen bromide in the presence of anhydrous potassium carbonate in dry acetone giving rise to 7-hydroxy-chromeno-(3′ : 4′ : 2 : 3)-chromone (III).

Experimental

2-Ethoxymethyl-7-hydroxy isoflavone (*I*)

ω-Phenyl resacetophenone (5 g.) in dry pyridine (30 c.c.) was treated with ethoxy acetyl chloride (10 c.c.) at 0°. The product of condensation was worked up after 24 hours in the manner reported earlier[4] for acetyl chloride. The intermediate diketone could not be obtained crystalline and pure. Hence it was refluxed with 10% aqueous sodium carbonate (200 c.c.) for 2 hours. The solution was cooled, filtered, and the filtrate acidified with dilute hydrochloric acid. The sticky solid that separated out was extracted with ether and the extract dried over anhydrous magnesium sulphate. The residue left after the removal of the solvent crystallised from a mixture of ether and light petroleum and finally from ether as colourless rectangular prisms, m.p. 146–47° (3 g.) (Found: C, 72·9; H, 5·2; $C_{18}H_{16}O_4$ requires C, 73·0 ; H, 5·4%). The mother liquor on concentration yielded the original ketone (1·2 g.).

2-Bromo-methyl-7-hydroxy isoflavone

The above isoflavone (I) (1 g.) was dissolved in glacial acetic acid (10 c.c.) and hydrobromic acid in glacial acetic acid (50%; 10 c.c.) added. After keeping at room temperature for 12 hours a further quantity of hydrobromic acid (50%; 10 c.c.) was added and the mixture refluxed on a water-bath for 45 minutes. Ice-cold water was added and the solid that separated out was filtered and dried. It crystallised from a mixture of ethyl acetate and light petroleum as tiny rectangular prisms, m.p. 246–47° (0·8 g.). Mixed m.p. with an authentic sample[7] was undepressed.

2-Ethoxymethyl-7-hydroxy-2′-methoxy isoflavone (*II a*)

2 : 4-Dihydroxy-2′-methoxy phenyl benzyl ketone (5 g.) in dry pyridine (30 c.c.) was condensed with ethoxy acetyl chloride (10 c.c.) at 0° and the product worked up as in the previous case. 2-Ethoxymethyl isoflavone (II *a*) crystallised from a mixture of ether and light petroleum and finally from ether as colourless rhombohedral prisms, m.p. 168–70° (3·2 g.) (Found:

C, 69·3; H, 5·7; $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%). The mother liquor on concentration gave the original ketone (1 g.).

2-Bromo-methyl-7 : 2′-dihydroxy isoflavone (II b)

The above isoflavone (II *a*) (1 g.) was treated with glacial acetic acid and hydrobromic acid as done in the simpler case. The product crystallised rom a mixture of ethyl acetate and light petroleum and finally from ethyl acetate as colourless stout rectangular prisms, m.p. 213–14° (decomp.) (0·8 g.) (Found: C, 55·4; H, 3·5; $C_{16}H_{11}O_4Br$ requires C, 55·3; H, 3·2%).

7-Hydroxy-chromeno-(3′ : 4′ : 2 : 3)-chromone (III)

The above isoflavone (II *b*) (0·3 g.) was dissolved in dry acetone (100 c.c.), freshly ignited potassium carbonate (3 g.) added and the mixture refluxed for 4 hours. More potassium carbonate (3 g.) was now added and the refluxing continued for 6 hours more. Acetone was distilled off, the residue dissolved in water and acidified with dilute hydrochloric acid. The solid product crystallised from alcohol as colourless needles, m.p. 240–42° (decomp.) (0·2 g.). Mixed m.p. with an authentic sample[1] was undepressed. The acetate obtained by the acetic anhydride-pyridine method also agreed in its melting with the authentic sample.

SUMMARY

By the use of ethoxy acetyl chloride and pyridine at 0°, 7-hydroxy-chromeno-(3′ : 4′ : 2 : 3)-chromone has been synthesised much more conveniently than by the earlier methods reported in the literature.

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ON THE DIFFRACTION OF LIGHT BY PROGRESSIVE AND STANDING SUPERSONIC WAVES

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1. Introduction

Using a method based on series expansions in Mathieu functions, we have shown the following property concerning the intensities of the lines of the spectra caused by the diffraction of light by supersonic waves at normal incidence of the light[1]: if only the zero and first orders are visible, the values of the intensities of the orders $+1$ and -1 for standing supersonic waves are half the values of the intensities of the same orders in the case of progressive sound waves.

A confirmation of this property was found in the experiments of Sanders,[2] which give a systematic comparison between the diffraction spectra caused by progressive and standing supersonic waves.

The purpose of the present paper is to deduce this property from the generalised theory of Raman and Nath.[3]

2. The Results of Nagendra Nath for Progressive Sound Waves[4]

According to the generalised theory of Raman and Nath the amplitudes of the diffracted light waves satisfy the following system of difference differential equations

$$2\frac{d\phi_n}{d\xi} - (\phi_{n-1} - \phi_{n+1}) = in^2\rho\phi_n \qquad (n = -\infty, \ldots, +\infty), \tag{1}$$

with the boundary conditions

$$\phi_0(0) = 1, \ \phi_n(0) = 0 \quad (n \neq 0); \tag{2}$$

where

$$\xi = \frac{2\pi\mu z}{\lambda},$$

z = the width of the sound field along the direction of the incident light,

$$\rho = \frac{\lambda^2}{\mu\mu_0\lambda^{*2}},$$

λ = the wave-length of the incident light in vacuum,

λ^* = the wave-length of the supersonic waves in the considered medium,

μ_0 = the refractive index of the undisturbed medium,

μ = the maximum variation of the refractive index.

Nagendra Nath has further shown,[4] that if the parameter $\rho \gg 1$, only a small number of orders will appear. In the case that only zero and first orders are visible, the system (1) becomes,

$$\begin{cases} \dfrac{d\phi_0}{d\xi} + \phi_1 = 0 \qquad (\phi_{-1} = -\phi_1) & (3\,a) \\ 2\,\dfrac{d\phi_1}{d\xi} - \phi_0 = i\rho\phi_1 & (3\,b) \end{cases}$$

and its solution satisfying the boundary conditions (2) is

$$\phi_0 = \left[1 - \frac{8}{\rho^2+8}\sin^2\left\{\frac{(\rho^2+8)^{\frac{1}{2}}}{4}\,\xi\right\}\right]^{\frac{1}{2}} \times \exp\left[\,i\left\{\frac{\rho\xi}{4} - \tan^{-1}\left(\frac{\rho}{(\rho^2+8)^{\frac{1}{2}}}\tan\frac{(\rho^2+8)^{\frac{1}{2}}}{4}\,\xi\right)\right\}\right] \qquad (4\,a)$$

$$\phi_1 = \frac{2}{(\rho^2+8)^{\frac{1}{2}}}\sin\left\{\frac{(\rho^2+8)^{\frac{1}{2}}}{4}\,\xi\right\}\exp\left\{\,i\rho\,\frac{\xi}{4}\right\}. \qquad (4\,b)$$

The first order intensity is then

$$I_1 = \frac{4}{\rho^2+8}\sin^2\left\{\frac{(\rho^2+8)^{\frac{1}{2}}}{4}\,\xi\right\} \approx \frac{4}{\rho^2}\sin^2\frac{\rho}{4}\,\xi. \qquad (5)$$

3. The Results for Standing Sound Waves

In the case of standing sound waves the system determining the amplitudes of the different diffracted orders is[3]

$$2\,\frac{d\phi_n}{d\xi} - \sin\epsilon\,(\phi_{n-1} - \phi_{n+1}) = in^2\rho\phi_n \qquad (n = -\infty, \ldots, +\infty) \qquad (6)$$

with

$$\epsilon = 2\pi\nu^* t, \qquad (6\,a)$$

ν^* = the frequency of the sound waves.

The boundary conditions still are

$$\phi_0(0) = 1,\ \phi_1(0) = 0. \qquad (7)$$

If orders higher than the first are to be neglected, the system (6) becomes explicitly,

$$\begin{cases} \dfrac{d\phi_0}{d\xi} + \phi_1 \sin \epsilon = 0 & (8\,a) \\ 2\,\dfrac{d\phi_1}{d\xi} - \phi_0 \sin \epsilon = i\rho\phi_1. & (8\,b) \end{cases}$$

Making the substitution

$$\zeta = \xi \sin \epsilon \qquad (9\,a)$$

$$\sigma = \rho/\sin \epsilon, \qquad (9\,b)$$

we can write this system as

$$\begin{cases} \dfrac{d\phi_0}{d\zeta} + \phi_1 = 0 & (10\,a) \\ 2\,\dfrac{d\phi_1}{d\zeta} - \phi_0 = i\sigma\phi_1, & (10\,b) \end{cases}$$

which has the same form as the system (3 *a*, *b*) and, of course, the same solution, if one respectively replaces ξ and ρ by ζ and σ. Formula (4 *b*) giving the first order amplitude thus becomes,

$$\phi_1 = \frac{2}{(\sigma^2+8)^{\frac{1}{2}}} \sin \left\{ \frac{(\sigma^2+8)^{\frac{1}{2}}}{4}\ \zeta \right\} e^{\frac{i\sigma\xi}{4}}$$

$$= \frac{2 \sin \epsilon}{(\rho^2 + 8 \sin^2 \epsilon)^{\frac{1}{2}}} \sin \left\{ \frac{(\rho^2 + 8 \sin^2 \epsilon)^{\frac{1}{2}}}{4}\ \xi \right\} e^{\frac{i\rho\xi}{4}}$$

or taking into account, that $\rho \gg 1$

$$\phi_1 \approx \frac{2 \sin \epsilon}{\rho} \sin \left(\frac{\rho}{4}\,\xi \right) e^{\frac{i\rho\xi}{4}} = \frac{e^{i\epsilon} - e^{-i\epsilon}}{i\rho} \sin \left(\frac{\rho}{4}\,\xi \right) e^{\frac{i\rho\xi}{4}}. \qquad (11)$$

This wave is thus splitted in two waves, having frequency-changes of the amount $+\nu^*$ and $-\nu^*$. The amplitude of the wave undergoing a frequency-change $+\nu^*$ is $\mathcal{A}_+ = (1/i\rho) \sin (\rho\xi/4) \exp (i\rho\xi/4)$, while the amplitude of the wave having a frequency-change $-\nu^*$ is $\mathcal{A}_- = (-1/i\rho) \sin (\rho\xi/4) \exp (i\rho\xi/4)$. So the total intensity of the first order becomes

$$I_1(\xi) = \mathcal{A}_+\mathcal{A}_+^* + \mathcal{A}_-\mathcal{A}_-^* = \frac{2}{\rho^2} \sin^2 \frac{\rho\xi}{4}. \qquad (12)$$

The property stated in the introduction now follows immediately from comparison of the formulæ (5) and (12).

4. REMARKS

(1) If $\sin \epsilon = 0\,(t = m/2\nu^*)$, it is seen from the system $(8\,a,\ b)$, that $\phi_0 = \text{constant} = 1$ and $\phi_1 = \text{constant} \times \exp(i\rho\xi/2) = 0$, this last constant being zero according to the boundary conditions (7).

(2) The formula (12) may also be obtained in another way, which does not take account of the spectral character of the different orders. From the formula (5) the first order intensity in the case of standing sound waves may be written

$$I_1(\zeta) = \frac{4}{\sigma^2+8}\sin^2\left\{\frac{(\sigma^2+8)^{\frac{1}{2}}}{4}\,\zeta\right\} = \frac{4\sin^2\epsilon}{\rho^2+8\sin^2\epsilon}\sin^2\left\{\frac{(\rho^2+8\sin^2\epsilon)^{\frac{1}{2}}}{4}\,\xi\right\}$$

$$\approx \frac{4\sin^2\epsilon}{\rho^2}\sin^2\frac{\rho}{4}\,\xi \qquad (\rho \gg 1).$$

This intensity is depending periodically on time, so that only the mean intensity will be observed experimentally. This mean value is given by

$$I_1(\xi) = \overline{I_1(\zeta)} = \frac{4}{\rho^2}\sin^2\left(\frac{\rho}{4}\,\xi\right)\frac{1}{\tau^*}\int_0^{\tau^*}\sin^2 2\pi\nu^* t\,dt = \frac{2}{\rho^2}\sin^2\frac{\rho}{4}\,\xi$$

(τ^*= the period of the sound waves), which is the value given by (12).

5. SUMMARY

It has been shown that the following property of the spectrum of the diffraction of light by supersonic waves, in which orders higher than the first are missing, can easily be deduced from the generalised theory of Raman and Nath if $\rho \gg 1$: the intensity of the first orders in the case of standing sound waves has half the value of the intensity of the same orders in the case of progressive sound waves.

The author wishes to express his thanks to Professor Dr. M. Nuyens for the valuable discussions he had with him.

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ACETYLATION OF TAMARIND SEED JELLOSE

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Tamarind seed jellose is a polysaccharide* which is composed of galactose, xylose and glucose in the ratio of 1 : 2 : 3.[1, 2] The repeating unit of the macromolecule has been recently shown to have the following structure, containing 16 free hydroxyl groups.[3]

```
                X
                1      G   = Glucose
                2      Ga  = Galactose
        Ga      X      X   = Xylose
        1       1
        6       6
---------4G1, 4G1, 4G1,---------
```

The acetylation of the substance has been carried out under the same conditions as those adopted for starch,[4] and the results are reported in this paper.

Jellose, like starch, undergoes progressive acetylation, depending upon the acetylating agent and the conditions of the experiment. If one hydroxyl in every one of the six saccharide rings of the hexasaccharide unit undergoes acetylation, a hexaacetate results corresponding to the monoacetyl derivative of starch. If two of the hydroxyls in every one of the six saccharide rings are acetylated, the product is a duodecaacetate corresponding to the diacetate of starch. If all the hydroxyls are acetylated, a hexadecaacetate forms, which corresponds to the triacetate of starch. Corresponding to these stages, the hexaacetyl, duodecaacetyl and hexadecaacetyl derivatives of jellose have

* In a recent note (*Curr. Sci.*, 1955, **24**, 235) Savur has claimed to have isolated from tamarind kernel powder three distinct types of polysaccharide fractions, differing in their solubility and power of gelation. The author appears to suggest that the above fractions are different chemical entities. However, it is very likely that they may be the same polysaccharide existing in different degrees of polymerisation. The material used in the present investigation as also that employed for the earlier constitutional studies (Rao, P. S. and White, E. V., *J. Am. Chem. Soc.*, 1953, **75**, 2617) was prepared and purified according to the procedure described earlier (Rao, P. S., Ghose, T. P. and Krishna, S., *J. Sci. and Ind. Res.*, 1946, **4**, 705). It did not show any heterogeneity on repeated precipitations from dilute aqueous solutions by means of alcohol, the purified product having a specific rotation of 71·4° in 0·25 per cent. aqueous solution and a pentosan content of 30·5 per cent. (Rao, P. S. and Krishna, S., *Curr. Sci.*, 1946, **15**, 133).

been obtained. It may, however, be noted that the reaction need not invariably take place in the stepwise manner indicated; in fact, as in the case of starch, intermediate acetyl derivatives are also formed.

It may be mentioned that the polysaccharide undergoes acetylation even with boiling glacial acetic acid in the presence of anhydrous sodium acetate (*cf.* starch[5]) and the extent of acetylation depends on the duration of the treatment.

The acetyl derivatives are as a class insoluble in water and, some, even in organic solvents. The solubility appears to depend not only on the extent of acetylation but also on the degree of depolymerisation that the molecule undergoes during the chemical treatment. The insoluble products can be rendered soluble in organic solvents by treatment with a hot mixture of sulphuric and glacial acetic acids. In appropriate solvents some of the acetyl derivatives yield fairly strong, flexible, glossy and transparent films which adhere to glass, wood and metal surfaces. From this point of view the product obtained by the action of boiling acetic acid is particularly good. Further, some of the acetates, on account of their wide melting-range, may be useful as thermoplastic resins.

EXPERIMENTAL

Action of glacial acetic acid.—Dry jellose (10 g.) was refluxed with 200 c.c. of glacial acetic acid and one gram of anhydrous sodium acetate for varying periods. After each treatment the mixture was poured on crushed ice and the resulting solid was filtered, boiled with small quantities of fresh water to remove any unreacted jellose, cooled, filtered, washed with alcohol and finally dried in vacuum. The properties of the different products are given in the following table:—

TABLE I

Length of treatment	Acetyl value	Properties
12 hours	12·39%	Insoluble in water and all the ordinary organic solvents.
24 hours	16·58%	Behaves similar to the previous case but swells in glacial acetic acid.
36 hours	19·98%	Soluble in alcohol, pyridine and dilute acetic acid but not in water, acetone and chloroform.

In the first two cases (boiling for 12 and 24 hours) the yields were not high, because the products were contaminated with considerable quantities of unreacted jellose. In the third case, however, the yield was 8 g. from 10 g. of the jellose. In this treatment the reaction product went into solution in the acetic acid and did not separate out on simple dilution, but only on saturation with sodium chloride. Its solutions on slow evaporation left fairly strong, pliable and transparent films. It softened at 270° and became dark at higher temperatures, but did not melt below 320°.

Jellose hexaacetate.—The jellose was initially gelatinized by treatment with formic acid. Dry jellose (10 g.) was gradually added to 100 c.c. of 90 per cent. formic acid with continuous stirring. The substance immediately swelled, forming a thick viscous solution. An analysis of the isolated product showed that the formic acid reacted with the jellose, converting the latter into the hexaformyl derivative [$(\alpha)_D^{25°}$ in formic acid solution ($c = 0{\cdot}3\%$) = + 46·3°; softens at 260°, swells enormously on further heating but does not melt below 320°]. Continuing the stirring, acetic anhydride (100 c.c.) was added dropwise. Since carbon monoxide was evolved as a result of the decomposition of formic acid, the operation was carried out in a fume chamber. During the reaction the temperature rose gradually and had to be controlled by means of crushed ice. When the addition of acetic anhydride was over, the reaction mixture was cooled and treated with ice-cold water. On vigorous stirring a faintly brownish solid separated. The yield was 12 g. It was insoluble in alcohol, acetone, chloroform, pyridine, etc., and was moderately soluble in formic acid, in which $[\alpha]_D^{25°}$ was + 59·4° ($c = 1\%$). It softened at 230° and melted with decomposition at 280°. This corresponded to the hexaacetyl derivative of the jellose (Found:—$COCH_3$, 22·4; $[C_{34}H_{50}O_{28}\ (COCH_3)_6]_n$ requires—$COCH_3$, 22·2%).

In the above experiment smaller quantities of formic acid could be used for swelling the jellose but the difficulty was as regards the stirring. Even in 10 per cent. concentration, the jellose formed a thick dough with the acid. However, when the formic acid was sprayed on the jellose triturating in a mortar, the swelling was quite rapid and efficient. By this means the weight of formic acid necessary for swelling could be reduced to an amount equal to the weight of jellose.

Jellose duodecaacetate.—The experiment was carried out as in the previous case but with the difference that acetic anhydride containing 1 per cent. of concentrated sulphuric acid was used instead of acetic anhydride alone, and the product was duodecaacetate. The isolation and purification were done

as in the previous case (Found:—$COCH_3$, 36·0; $[C_{34}H_{44}O_{28}(COCH_3)_{12}]_n$ requires—$COCH_3$, 36·4%). The yield was 12·5 g. from 10 g. of the jellose. It was soluble in acetone, acetic acid and pyridine and was insoluble in chloroform and alcohol. In pyridine solution (0·75%), $[\alpha]_D^{25°}$ was + 51·6°. Softening at 240°, it did not melt below 320°.

Jellose hexadecaacetate.—If in the above experiment the reaction mixture was heated at 95° C. for two hours with continuous stirring, the completely acetylated product was obtained. During the first hour the temperature was slowly raised to 95° and was subsequently maintained thereat for the rest of the period. On dilution with ice-cold water and stirring, the acetyl derivative separated out. The yield was 16·6 g. from 10 g. of the jellose. The product was soluble in acetic acid, acetone, chloroform and pyridine but not in alcohol, and exhibited a specific rotation of + 28·5° in pyridine solution (c = 0·5%). It softened at about 240°, assumed a dough-like structure at 280° and did not melt below 320°. It was largely the completely acetylated derivative (Found:—$COCH_3$, 44·3; $[C_{34}H_{40}O_{28}(COCH_3)_{16}]_n$ requires—$COCH_3$, 43·4%).

Conversion of insoluble into soluble acetates.—The insoluble acetate (10 g.) was suspended in 100 c.c. of glacial acetic acid containing 1·5 per cent. of concentrated sulphuric acid, and the suspension was heated on an oil-bath. The temperature was slowly raised to 95° during the course of an hour and the heating was continued for another hour at the same temperature. The mixture was then diluted with ice-cold water, whereupon the " soluble " acetate separated (yield: 9·5 g.).

Experiments on the utilisation of the acetates.—Since the melting range of the acetates is fairly wide, covering nearly 60° from the softening point to the formation of the melt, the substances, it was felt, might be useful as thermoplastic materials. However, preliminary experiments on moulding of the esters at temperatures just a little above the softening points indicated that the casts were rather brittle, though the surface was glossy. Addition of plasticisers like camphor, phthalic anhydride and esters of phthalic acid in varying amounts improved the properties of the casts to different degrees. Phthalic anhydride and esters of phthalic acid (25 per cent. addition) gave the best results but even then the casts were not sufficiently strong and tough. In these experiments the duodeca ester gave much better results than the other acetates. The addition of cellulose acetate by about 25 per cent. improved the strength of the jellose acetate moulds (*cf.* starch esters[4]).

The films formed by the evaporation of the solutions of the hexadeca-acetate, though transparent and glossy, were very brittle. Addition of plasticisers did not improve the properties appreciably. On the other hand the films formed from the duodeca ester were strong and tough and plasticisers (the anhydride and the esters of phthalic acid), when added in about 25 per cent. further improved the properties. Being transparent, glossy and water-resistant, the films may find application in the preparation of water-proof covers. In this connection special mention may be made of the lower acetylated products obtained by the treatment of the jellose with boiling glacial acetic acid for 36 hours. Their films from pyridine solution were pliable, fairly strong and transparent.

When applied to wood in pyridine solution the coatings of plasticised acetates resembled varnishes. These coatings adhere to glass and metals as well, and on drying, particularly at higher temperatures, they become flexible and impermeable to moisture. A suitable concentration in these experiments was found to be 5 per cent.

Summary

The hexa, duodeca and hexadeca acetyl derivatives of tamarind seed jellose have been prepared by treatment with acetic anhydride under different conditions. Boiling glacial acetic acid also effects partial acetylation.

Some of the acetyl derivatives in appropriate solvents give fairly strong, flexible, glossy and transparent films, which adhere to glass, metallic and also wooden surfaces. They may also be useful as thermoplastic resins on account of their wide melting range.

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EFFECT OF LUNAR ATMOSPHERIC TIDE ON THE MESON INTENSITY AT KODAIKANAL

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Abstract

The lunar semidiurnal variation in the meson intensity at Kodaikanal has been determined by the Chapman-Miller method of analysis from bihourly records of the cosmic ray meson intensity registered by three-fold coincidences for two consecutive groups of data, each extending over a period of 18 months. The former period gives a result about two to three times the probable error and can be taken to be significant.

While the correlations between the solar diurnal variation of meson intensity and barometric pressure are high and negative, the corresponding correlations between the lunar semidiurnal variations of meson intensity and barometric pressure are positive. The results obtained at Kodaikanal agree with those of Duperier obtained at London.

But the latter period does not give any significant result outside the probable error. Hence further investigation has to be continued.

I. Introduction

The lunar tide produced in the atmosphere, though small compared to its counterpart solar tide, is nevertheless important. It is revealed in the lunar semi-diurnal variations of the barometric pressure,[1] of air temperature,[2] of the height of the E-layer,[3] of wind components,[4] of geomagnetic elements[5] and of the cosmic ray meson intensity registered at ground level.[6] In addition to producing a mass absorption effect in cosmic rays, it is to be expected that the pressure oscillation would result in a vertical shift of the isobaric levels. If this shift is appreciable at the height where the bulk of the cosmic ray mesons are supposed to originate, there would result an increase or decrease of the meson intensity at the ground level, depending on whether the level of formation goes down or up.

A study of the influence of the lunar tide in the atmosphere on the meson intensity of cosmic rays is important not only for understanding the atmospheric oscillations at various levels, but also for checking our current

theories on the transition effects of cosmic rays in our atmosphere. So far, the only determination of the lunar semidiurnal variation L_2 in meson intensity is the one reported by Duperier[6] from data collected at London. He has reported an amplitude twice the probable error, and while this is indicative of the existence of L_2, the evidence is not conclusive.

Duperier is reported to have given further results of the effect of atmospheric lunar tide on the cosmic ray intensity, at the Cracow conference in 1947. His later result is reported to have an amplitude nearly thrice the probable error. The positive correlation between the L_2 for meson intensity and L_2 for barometric pressure is also surprising, in contrast to the negative effect observed in the solar daily variation. Since at low latitudes, the lunar and solar daily variations of barometric pressure are much larger than at high latitudes, it is particularly appropriate to study their effects on meson intensity at an equatorial station like Kodaikanal. (Latitude 10° 14′ N., Longitude 77° 28′ E., Geo-magnetic Latitude 1° N., Altitude 7,688 ft. above sea-level).

II. Procedure

The lunar daily variations are generally masked by irregular variations and by solar daily variations which are comparatively larger. However, the elegant method developed by Chapman and Miller[7] enables the determination of the effect of the lunar atmospheric tide on the meson intensity. The cosmic ray meson intensity has been collected at Kodaikanal during the period May 1952 to December 1953 by one of the authors (D. V.) and from January 1954 to June 1955 by the other (T. S. G. S.). Separate records have been obtained for vertical intensity M_1 of radiation penetrating 7 cm. of lead absorber and for intensity M_2 of radiation penetrating 15 cm. of lead absorber. Both M_1 and M_2 correspond principally to intensity of mesons, though the latter contains relatively more energetic particles than the former. The mean bihourly rate for meson intensity is about 4,000 triple coincidences per bihour per telescope.

Though hourly photographs were available only bihourly data have been utilised, because, this reduces the labour to half with hardly any loss in the accuracy of the results. The days are sorted out according to their μ values, where μ refers to the lunar phase. In the course of a synodic month, μ decreases from 24 to 0. $\mu = 24$ or 0 is new moon, $\mu = 18$ is first quarter, $\mu = 12$ is full moon and $\mu = 6$ is the last quarter. For the Chapman-Miller-method of analysis, only 12 groups are needed. Days of μ value r are combined with days of μ value $(r + 12)$. Incomplete daily sequences have not been taken into consideration and only days for which there is no

break have been used. The daily sequence consists of thirteen bihourly terms, the thirteenth being the value for the initial bihour of the succeeding day. Each daily sequence is a unit and can be combined with other daily sequences. Summation of the sequences corresponding to the twelve groups of μ is carried out. This method of using a thirteen term sequences for each day allows for a correction to be applied for the average non-cyclic change. The analysis has been done on the same lines as described by Tschu.[8]

A preliminary calculation with the data of one of the authors (D. V.) showed that when all the days are used, the probable error turns out to be very large. It is therefore necessary to select the days. This procedure is necessary as irregular large fluctuations tend to mask the small periodic variation under search as has been pointed out by Chapman. For this purpose, σ, the expected standard deviation in a bihourly estimate, is calculated. $\sigma = \sqrt{n}$, where n is the mean bihourly counts. The actual bihourly deviation, Δ, from mean of each daily sequence is then compared with σ to provide a criterion for sorting the daily sequences in terms of the degree of disturbance.

The sequences are sorted out into three groups $\Delta > 2\sigma$, $\Delta > 3\sigma$, and $\Delta > 5\sigma$ respectively. The major portion of the data falls within the second group. The number of days falling within the first group are unevenly distributed among the various μ groups and hence is not useful for study. When the third group is taken, the probable error turns out to be large. Hence it was found that days for which $\Delta > 3\sigma$ would be a good criterion for selection.

In the process of calculating the lunar semidiurnal variation L_2, the solar semidiurnal variation S_2 is also derived. This can be compared with the value derived directly from the 12 solar bihourly deviations from mean for sequences for all μ values grouped together.

For atmospheric pressure only days in which the difference range did not exceed 3 millibars have been taken into consideration. Although the lunar semidiurnal variation of the barometric pressure at Kodaikanal has already been calculated,[9] it has been redetermined for the period of experimentation, as a check on our method of calculation.

An alternate method of determining the lunar semidiurnal variation L_2 in meson intensity and in the barometric pressure at Kodaikanal has also been attempted. The daily sequences are separated into 24 μ groups instead of 12·0 hour of a day for which μ is 24 is nearly equivalent to 2 hours of a day for which μ is 22 and is nearly equivalent to 4 hours of a day for

which μ is 20 and so on. So the data corresponding to 0 hour of days of $\mu = 24$ are combined with those of 2 hours of days of $\mu = 22$ and then with those of 4 hours of days of $\mu = 20$ and so on. Similarly for all other bihours, addition is done to give the net summation of the group sequences according to lunar hours 0, 2, 4, etc.

The the odd group, namely days of μ values 23, 21, ..., 1, are taken and addition is carried out in the same way as pointed out in the previous para. But 2 hours of a day for which μ is 23 will be be equivalent to 1 hour of a day for which μ is 24, 4 hours of a day of $\mu = 23$ will be equivalent to 3 hours of a day of $\mu = 24$ and so on. Hence from this group we get the net summation of the group sequences according to odd lunar hours 1, 3, 5, etc. These 24 values are subjected to Fourier Analysis to determine the second harmonic.

III. Results

A. *Data from May* 1952 *to December* 1953

Table I gives the distribution of the days according to μ groups, for meson intensity M_1 for $\Delta \geqslant 2\sigma$, $\Delta \geqslant 3\sigma$, and $\Delta \geqslant 5\sigma$; for M_2 for $\Delta \geqslant 2\sigma$, $\Delta \geqslant 3\sigma$, and $\Delta \geqslant 5\sigma$; for $(M_1 + M_2)$ for $\Delta \geqslant 3\sigma$.

TABLE I

Distribution of days according to μ values

μ values		0 & 12	1 & 13	2 & 14	3 & 15	4 & 16	5 & 17	6 & 18	7 & 19	8 & 20	9 & 21	10 & 22	11 & 23	Total days
M_1	$\Delta \geqslant 2\sigma$..	6	10	12	16	14	14	12	15	11	18	9	15	152
	$\Delta \geqslant 3\sigma$..	30	23	29	29	31	31	30	33	32	38	25	33	364
	$\Delta \geqslant 5\sigma$..	34	41	37	39	38	37	38	45	38	43	34	39	463
M_2	$\Delta \geqslant 2\sigma$..	12	14	13	12	12	17	19	21	12	15	19	15	181
	$\Delta \geqslant 3\sigma$..	26	27	28	29	29	33	33	37	32	35	32	26	367
	$\Delta \geqslant 5\sigma$..	28	39	32	40	32	39	36	41	38	43	33	24	425
(M_1+M_2)	$\Delta \geqslant 3\sigma$	56	50	57	58	60	64	63	70	64	73	57	59	731

Table II gives the determination of 1_2, the amplitude and λ_2, the phase of the semidiurnal variation L_2 for meson intensity M_1, M_2 and $(M_1 + M_2)$ for the various cases and for pressure P. The probable errors are also given in the table. It can be seen that only for meson intensity M_1 for $\Delta \geqslant 3\sigma$,

TABLE II

L_2

		l_2	P.E.	λ_2
		%	%	
	$\Delta \geqslant 2\sigma$	0·07	0·07	−34° 34′
M_1	$\Delta \geqslant 3\sigma$	0·15	0·05	− 9° 2′
	$\Delta \geqslant 5\sigma$	0·12	0·05	8° 1′
	$\Delta \geqslant 2\sigma$	0·08	0·07	−54° 29′
M_2	$\Delta \geqslant 3\sigma$	0·04	0·04	−26° 35′
	$\Delta \geqslant 5\sigma$	0·05	0·05	1° 57′
$(M_1 + M_2)$	$\Delta \geqslant 3\sigma$	0·09	0·04	−14° 39′
P		40 microbars	12·8	31° 16′

M_1 = Meson passing through 7 cm. of lead absorber.
M_2 = Meson passing through 15 cm. of lead absorber.
P = Barometric pressure.
Δ = Degree of disturbance of the days chosen.
P.E. = Probable error.
l_2 = Amplitude of lunar second harmonic of meson, and pressure.
λ_2 = Phase of lunar second harmonic of meson and pressure.

M_1 for $\Delta \geqslant 5\sigma$ and for $(M_1 + M_2)$ for $\Delta \geqslant 3\sigma$, and for pressure, are the results fairly significant.

Fig. 1 shows on a lunar 12-hourly harmonic dial, the determination of L_2 for meson intensity M_1, M_2, $(M_1 + M_2)$ and pressure P. The probable error circles are also indicated at the end of the vectors.

Table III shows the value of solar semidiurnal variation S_2 derived during the process of calculating L_2, along with the value derived directly by the usual method without separation of the days according to μ groups. S_2 refers to the solar semidiurnal amplitude and ψ_2 to the phase.

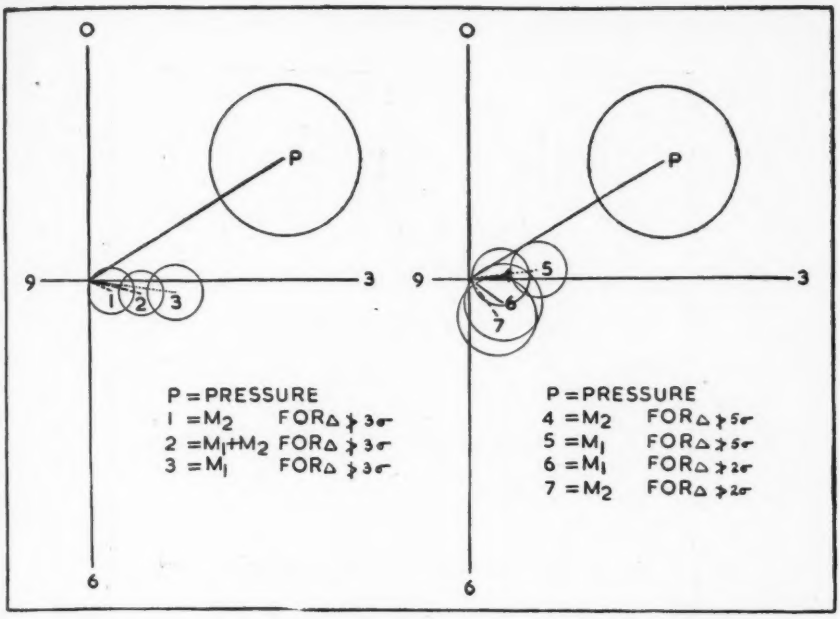

FIG. 1. Lunar 12-hourly harmonic dial showing the lunar semidiurnal component for meson intensity M_1, M_2 and $(M_1 + M_2)$, and pressure P.

TABLE III

S_2

	s_2	ψ_2
A	·39%	−59°
B	·43%	−68°

s_2 = Amplitude of solar semidiurnal component of meson.
ψ_2 = Phase of solar semidiurnal component of meson.
A = Derived during the course of the derivation of the lunar tide.
B = Derived in the usual way, without separating the data according to lunar phase angle.

The 24 values obtained for M_1 and $(M_1 + M_2)$ for $\Delta \gtrless 3\sigma$ and for pressure P are smoothened by taking moving average of three consecutive values. These smoothened daily variation curves according to lunar hours

are shown in Fig. 2. The positive correlation between the lunar daily variations of meson intensity and pressure is clearly visible.

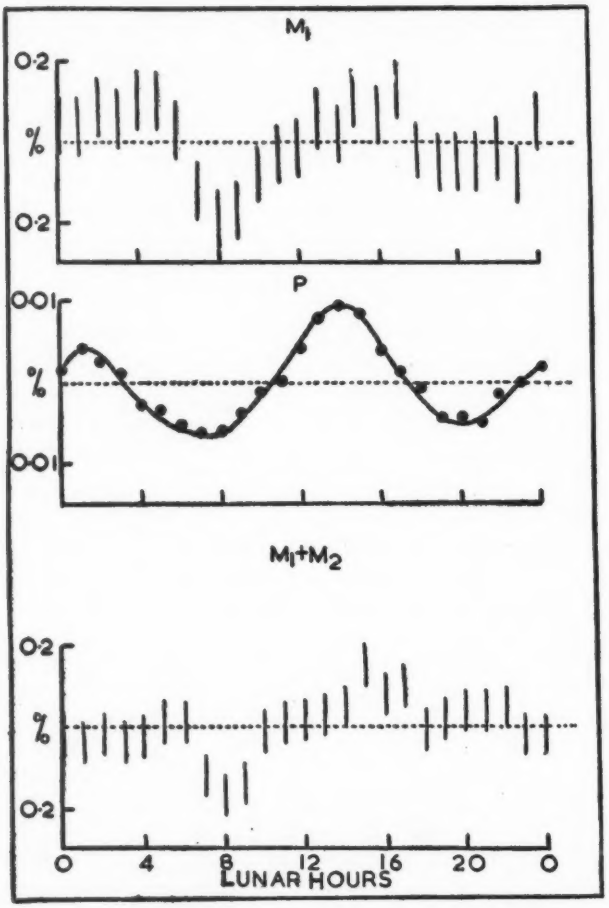

FIG. 2. Lunar daily variation curves of meson intensity M_1, $(M_1 + M_2)$, and pressure P after taking the moving average of three consecutive hourly values.

As a check on the Chapman-Miller method L_2 has been determined for meson intensity M_1 for $\Delta \gtrsim 3\sigma$ and pressure P by the alternate method. This is shown in Table IV. There is fair agreement between the two results.

Table V compares the study at Kodaikanal during the period May 1952 to December 1953, with Duperier's study at London during the period

TABLE IV

L_2

(Alternate Method)

	l_2	λ_2
M_1	0·14%	−21°
P	47 microbars	39°

TABLE V

	Greenwich	Kodaikanal
Meson s_2 ..	0·14%	0·43%
ψ_2 ..	−6°	−68°
Press. s_2 ..	0·22%	0·74%
ψ_2 ..	144°	132°
Meson l_2 ..	0·023%	0·15% for M_1, 0·09% for $(M_1 + M_2)$
λ_2 ..	160°	−9° for M_1, −15° for $(M_1 + M_2)$
Press. l_2 ..	0·009%	0·03%
λ_2 ..	114°	39°
Meson s_2/l_2 ..	6	3 for M_1, 5 for $(M_1 + M_2)$
Press. s_2/l_2 ..	24	25
$\gamma_{L(MP)}$ ..	0·69	0·67 for M_1, 0·59 for $(M_1 + M_2)$
$\beta_{L(MP)}$ ..	1·76% per mm.	3·35% per mm. for M_1, 1·77% per mm. for $(M_1 + M_2)$
$\gamma_{S(MP)}$ ..	−0·87	−0·95
$\beta_{S(MP)}$ ..	−0·55% per mm.	−0·54% per mm. for $(M_1 + M_2)$

s_2 = Amplitude of solar second harmonic.
ψ_2 = Phase of solar second harmonic.
l_2 = Amplitude of lunar second harmonic.
λ_2 = Phase of lunar second harmonic.
$\gamma_{L(MP)}$ = Lunar correlation coefficient between meson and pressure.
$\beta_{L(MP)}$ = Lunar pressure coefficient.
$\gamma_{S(MP)}$ = Solar correlation coefficient between meson and pressure.
$\beta_{S(MP)}$ = Solar pressure coefficient.

TABLE VI

L_2

(Chapman-Miller Method)

Meson		l_2	P.E.	λ_2
		%	%	
M_1	$\Delta \gtrless 3\sigma$	0·04	0·04	$\pi - 11°$
M_2	$\Delta \gtrless 3\sigma$	0·05	0·04	$\pi - 5°$
$(M_1 + M_2)$	$\Delta \gtrless 3\sigma$	0·04	0·04	$\pi - 7°$

TABLE VII

L_2

(Alternate Method)

Meson		l_2	λ_2
		%	
M_1	$\Delta \gtrless 3\sigma$	0·04	$\pi - 25°$
M_2	$\Delta \gtrless 3\sigma$	0·05	$\pi - 5°$
$(M_1 + M_2)$	$\Delta \gtrless 3\sigma$	0·04	$\pi - 13°$

May 1941 to April 1944. It is satisfactory that there is close similarity between the observed facts of the two places.

B. *Data from January* 1954 *to June* 1955

Only days for which Δ did not exceed 3σ are chosen. Table VI gives the L_2 determination for M_1, M_2 and $(M_1 + M_2)$ by the Chapman-Miller method, and Table VII gives the same by the alternate method. There is fair agreement between the two.

IV. DISCUSSION OF RESULTS AND CONCLUSION

A. *Data from May* 1952 *to December* 1953

For barometric pressure, the accurate determination of L_2 at Kodaikanal by S. K. Pramanik[9] from data covering a period of six years gives the

amplitude $1_2 = 52$ microbars and phase $\lambda_2 = 25°$. The agreement of these with the values determined for the limited period of 18 months during which the cosmic ray experiment at Kodaikanal was conducted by one of the authors (D. V.) is quite good.

The agreement between the values of the solar semidiurnal variation S_2 determined directly from bihourly deviations according to solar hours and those determined during the process of calculation of L_2 from data grouped according to lunar age as seen from Table III lends confidence to the L_2 determination.

From the comparison of the results obtained at Kodaikanal and at London, the following points emerge:—

(*a*) The l_2 and s_2 for pressure increase by about 3·3 times from latitude 52° N to latitude 10° N. In meson intensity the increases are of similar magnitude, being 3·9 for l_2 and 3·1 for s_2, for $(M_1 + M_2)$ with $\Delta \geqslant 3\sigma$. For M_1 with $\Delta \geqslant 3\sigma$, the increase in 1_2 is however larger.

(*b*) Both at London and Kodaikanal the correlation between the S_2 for meson intensity and S_2 for barometric pressure are high and negative. However the corresponding correlation between the L_2 for meson intensity and that for barometric pressure are positive, being $+0·69$ at London and $+0·67$ at Kodaikanal. Thus we have the curious result of having a negative barometric pressure coefficient for the solar tide S_2 and a positive barometric pressure coefficient for the lunar tide L_2. In discussing his result, Duperier has neglected this important feature. He has moreover treated the amplitudes of the S_2 and L_2 variations without consideration of the striking change in phase in relation to pressure oscillation in the two cases. Therefore his remarks directly comparing the nature of S_2 and L_2 variations in meson are not valid.

Duperier's later result does not differ appreciably from his earlier result, except that the latter is more significant. Therefore the conclusions drawn from his earlier result are valid for his later results also.

B. *Data from January* 1954 *to June* 1955

It is rather surprising that the analysis for this period has failed to give any significant results. All the amplitudes are of the same order as the probable error and as such no significant conclusions can be drawn from the same. It is difficult to understand why out of two consecutive periods, one should fail to give a significant result. It becomes therefore necessary to analyse further data before one can draw any definite conclusions about the effect of the lunar atmospheric tide.

We wish to express our thanks to Prof. V. Sarabhai for his continued interest in the problem and his helpful discussion. Our thanks are also due to Prof. Chapman for his valuable comments and to Prof. Wilkes who has been kind enough to verify some of the calculations by EDSAC method. Messrs. K. A. Gidwani, S. R. Thakore, S. Vishwanath and Miss Sushila S. Iyer have given computational assistance for which we are thankful. We are indebted to the Atomic Energy Commission, Government of India, for financial assistance.

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